İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

PREPARATION OF THERMOPLASTIC POLYURETHANE AND POLYTETRAFLOUROETHYLENE BLENDS AND THEIR CHARACTERIZATIONS

M.Sc. Thesis by
Ilker DEMIRYOL

Department : Polymer Science and Technology

Programme : Polymer Science and Technology

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İlker DEMİRYOL
(515051014)

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Supervisor (Chairman) : Prof. Dr. F.Seniha GÜNER (ITU)
Members of the Examining Committee : Prof. Dr. Nurseli UYANIK (ITU)
Prof. Dr. Sermet KABASAKAL(OGU)

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

TERMOPLASTİK POLİÜRETAN VE POLİTETRAFLOROETİLEN KARIŞIMLARIN HAZIRLANMASI VE KARAKTERİZASYONU

YÜKSEK LİSANS TEZİ
İlker DEMİRYOL
(515051014)

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Tez Danışmanı : Prof. Dr. F.Seniha GÜNER (İTÜ)
Diğer Jüri Üyeleri : Prof. Dr. Nurseli UYANIK (ITU)
Prof. Dr. Sermet KABASAKAL (OGU)

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FOREWORD

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İlker DEMİRYOL

Polymer Science and Technology

TABLE OF CONTENTS

Page

ABBREVIATIONS

TPU	**:** Thermoplastic Polyurethane
PTFE	**:** Polytetrafluoroethylene
MFI	**:** Melt Flow Index
TGA	**:** Thermal Gravimetric Analysis
SEM	**:** Scanning Electron Microscopy
DSC	**:** Differential Scanning Calorimetry

LIST OF TABLES

Page

LIST OF FIGURES

Page

LIST OF SYMBOLS

Φ = Filler volume fraction
σ = Tensile strength
K = Nicolais and Narkis adhesion coefficient of blends

PREPARATION OF THERMOPLASTIC POLYURETHANE AND POLYTHETRAFLUOROETHYLENE BLENDS AND THEIR CHARACTERIZATION

SUMMARY

Thermoplastic polyurethanes are most widely used for technical applications in industry and predominantly processed by injection molding. Blends are combination of two or more phases containing different polymers. Preparation of TPU/ PTFE blends have difficulties due to melting temperature differences of two materials. Therefore, fluoropolymer which can penetrate the other polymer's matrix are more favorable for TPU/PTFE blends.

Thermoplastic polyurethane (TPU) has good mechanical properties along with its elasticity and chemical resistance. Besides these properties TPU has gained an important position among other elastomers due to its easiness of processing, recyclability and reusage ability of faulty parts. The interest also increasing the replacement of the rubber elastomers with TPU due to mentioned reasons and environmental legislations. Thus, the more harsh applications are found, the more improved properties are required from TPU. This big interest forces chemists and engineers to improve properties of TPU. Some developments are able to be done by chemical structure. However, production costs, volume requirements and unavailable reactions make scientists to find another solutions. Blends are another common alternative to improve properties TPU. Properties can be combined which are belong to two or more polymers in one end product.

Polytetrafluoroethylene (PTFE) has a unique combination of properties such as low surface tension, low bulk shear strength and low coefficient of friction. These unique combination of properties make PTFE used in blends of many plastics.

In this study, the effects of different size and type of polytetrafluoroethylene (PTFE) on thermoplastic polyurethane (TPU) were investigated. The granular and micropowder PTFE types were used with TPU. Blends were premixed and specimens were produced by injection molding.

Working conditions were 210 ^{o}C in injection machine and 35 ^{o}C at mold, 55 bar pressure in injection and 50 bar at mold hold pressure. The samples were prepared by adding 2,5% and 5% of four different particle size PTFE to TPU.

TERMOPLASTİK POLİÜRETAN VE POLİTETRAFLOROETİLEN KARIŞIMLARIN HAZIRLANMASI VE KARAKTERİZASYONU

ÖZET

Termoplastik poliüretanlar(TPU), hem termoplastik hem de elastomer özelliğini aynı anda bünyesinde barındırmasından dolayı kullanım alanları her geçen gün artan malzemelerdir. TPU, endüstride çok yoğunlukla teknik uygulamalarda kullanılmaktadır. Elastikiyetlerinin yanında, iyi mekanik ve kimyasal dayanımları, bu malzemelerin belirgin özellikleridir. Bunun yanında, enjeksiyon ve ekstrusyon proseslerinde işlenme ve şekil verilebilme kolaylıkları, hatalı parçaların tekrar mekanik olarak parçalanarak kullanılabilmesi ve malzemenin geri-dönüştürülebilir olması TPU uygulamalarının artmasına neden olmaktadır. Böylece, daha yüksek derecede özellikler gerektikçe, TPU dan beklenen özellikler de artmaktadır. Bu büyük ilgi mühendisleri ve bilim adamlarını, TPU'nun özelliklerini geliştirmek için her geçen gün daha da zorlamaktadır. Kimyasal yapısında yapılacak değişikliklerle TPU özelliklerini artırmak için çalışmalar, üretim maliyetleri, mümkün olmayan veya kontrol edilmesi zor olan yan reaksiyonlar ve kapasite planlamaları sebebiyle, bilim adamlarını ve mühendisleri başka alternatif yöntemler bulmaya zorlamaktadır. Bu alternatif yöntemlerden en yaygını, polimer karışımlardır. Karışımlar iki veya daha fazla polimer/malzemenin farklı oranlarda karıştırılmasından oluşur. Karışımlarda, karışıma giren her malzemenin kendine ait özellikleri, karışımda içinde kendi özelliklerini gösterir. Böylece elde edilen karışım, karışım içindeki polimerlerin hepsinin kendilerine ait özelliklerini içerir. İstenilen özelliklere uygun olarak, karışım içindeki oranlar optimum seviyelerde belirlenir.

Bu çalışmada, değişik parçacık boyutunda ve çeşidindeki politetrafloroetilenlerin (PTFE) termoplastik poliüretanlara etkisi araştırılmıştır. Granül ve mikrotozlar TPU ile birlikte kullanılmıştır. Karışımlar, ön karıştırtırılmış ve karışım numuneleri enjeksiyon makinesi ile üretilmiştir.

Çalışma koşulları, 210 ^{o}C enjeksiyon sıcaklığı, 35 ^{o}C kalıp sıcaklığı, 55 bar enjeksiyon basıncı ve 50 bar ütüleme basıncıdır. Numuneler 2,5% ve 5% oranlarında, değişik parçacık boyutunda PTFE'nin TPU ya katılması ile hazırlanmıştır.

1. INTRODUCTION

Polyurethanes represent a large segment polymer used in high performance materials, such as coatings, adhesives, fibers, films and elastomers. Although, they are produced by a simple poly-addition reactions, there is a large number of possible final products. These possibilities are coming from ability to use combination of different raw materials and also changing of the properties according to the ratio of ingredients. This also increases the possibility of producing different materials with tailor-made properties. Thermoplastic polyurethanes (TPU) were the first homogenous elastomeric materials that could be processed by methods commonly used for the processing of thermoplastics. This processing is kind of flexibility that gives to TPUs more application opportunities in industry [1].

The credit for discovery of polyurethanes belongs to group led by Otto Bayer at the I.G. Farbenindustrie in Germany [2]. Today, it is well known that TPU has structure of combination of two segments that are named as hard segment and soft segment. The hard segment is formed by addition of the chain extender such as butadiene diol to the isocyanate. The soft segment consists of the flexible polyether or polyester chains that connect the two hard segments. The hard segment has higher melting point than soft segment. When the polymer is heated above the melting temperature of the hard segments, the polymer becomes a homogeneous viscous melt. Thus, viscous melt can be processed by usual methods used for plastics, such as extrusion, and injection molding. Cooling the melt results again a phase separation of soft and hard segments and the polymer develops its elastic properties [3].

In general, TPU is prepared from long chain polyols with the average molecular weight in the range of 600 to 4000, chain extenders with molecular weights in the range 61-400 and polyisocyanate. The choice of the components and their ratio determines the properties of the final product that range from soft and flexible to hard material [1].

Polytetrafluoroethylene (PTFE) is an important engineering material because serving of several unique properties such as low friction coefficient, high thermal chemical

and abrasion resistance and good lubricating properties together [4]. PTFE is polymerized from tetrafluoroethylene by radical free methods. The backbone is formed of carbon-carbon and carbon-fluorine bonds. Both are extremely strong bonds (C-C= 607 kJ/mole and C-F= 552 kJ/mole). Commercially, there are two processes for polymerization of PTFE. One is suspension polymerization that yield finer particles in dispersion. Other one is emulsion polymerization which is yield to granular PTFE resins. The polymer does not absorb significant amount of water and has low permeability to gases and moisture vapor. PTFE, like other fluoropolymers, has excellent heat resistance and can withstand temperatures up to 260 ^{0}C. Because of the high thermal stability, the mechanical and electrical properties of PTFE remain stable for long times at temperatures up to 260^{0}C. One disadvantage of PTFE is that it is extremely difficult to process by either extrusion or injection molding [5,6].

Polymer blend is a mixture of two or more polymers without chemical bonding. Thus, blend gains the properties of the each polymer and creates a new material. For example, TPU and PTFE have different unique advantages. The polymer blends of these materials show the combination properties of two materials [7].

The aim of this work is to produce TPU and PTFE blends by injection molding method. This study was carried out to determine the effects of different amount of addition and different size PTFE powders on TPU blends. The samples are investigated by mechanical properties and characterization methods.

2. THORETICAL PART

Polymer blend is a mixture contains two or more polymers with different weight percentage [8]. Polymer blending is designed to produce materials with optimized chemical, structural, mechanical, morphological and biological properties. Preparation of individual ratios of blended polymers requires many combinations and each combination has to be individually characterized [9]. Polymer blend performance depends on three factors: properties of ingredients, their content and morphology. Different strategies for the development of polymer blends have been used by the resin manufacturers and users. For resin manufacturer, blending provides to improve and broaden the resin performance and therefore increases its demand and sales. Here is the most important task is the development of blends with a full set of desired properties [10]. In addition, it is well known that polyurethane (PU) chemistry opened the new class of high performance materials such as coatings, adhesives, elastomers, fibers, foam etc. [11]. Increasing requirements are coming from TPU users due to replacement of PVC and rubber with TPU and also developments of new applications [12]. TPU blends are separated commonly in two types. One is TPU is added to other polymers to enhance their properties. Second is the addition polymers like PTFE, silicones and plasticizers or inorganic materials like molybdenum disulfide, glass fiber, nanoclay, flame retardants etc. to TPU [13,14]. PTFE is the one of the most versatile polymer. It can be both used itself and as polymer blends. It gives low friction coefficient, high abrasion resistance, increased dielectric strength, good barrier for water permeation and good burning resistance [15,16]. In this work, TPU and difference particle size PTFEs blends were produced by injection molding. Mechanical and thermal properties were investigated to understand the effects of the particle size and additional amount of PTFE.

2.1. Thermoplastic polyurethane (TPU)

Thermoplastic polyurethane (TPU) is one of the most versatile engineering thermoplastic with elastomeric properties. TPU combines the processability of

thermoplastic polymers with the mechanical properties of vulcanized rubber. They substitute other materials, polymers or elastomers, because of their low cost, higher elasticity, greater flexibility and toughness, fast elastic recovery, high load capacity and resistance to tear, oxidation and humidity. Another advantage is that they can be repeatedly melted and processed, due to the absence of the chemical networks normally present in rubber. TPU shows typical properties for elastomers in the solid state and able to be processed by methods used for thermoplastic materials at elevated temperatures [17,18].

TPU consist of two-phase morphology with hard and soft segments. Soft segment is made of either polyester or polyether. Hard segment is aromatic or aliphatic diisocyanate extended with short chain diol. The hard segments are generally dispersed in the amorphous phase. By varying the amount of hard and soft segments, properties of TPU can be varied. TPU can be also modified by blending with other polymers like polyacetal, polyamide, polystyrene, polycarbonate, polytetrafluoroethylene [19,20].

There are three main chemical classes of TPU:

• Polyester TPUs are compatible with PVC and other polar plastics. Offering value in the form of enhanced properties that they are unaffected by oils and chemicals, provide excellent abrasion resistance, offer a good balance of physical properties and are perfect for use in polyblends [21].

• Polyether TPUs are slightly lower in specific gravity than polyester and polycaprolactone grades. Polyether based TPUs have much lower viscosity than poltester based TPUs, because of the more mobile C-O-C bonds in soft segments. This gives higher melt flow ability and easier processing in injection molding to polyether based TPUs. They also offer low temperature flexibility and good abrasion and tear resilience. They are also durable against microbial attack, provide excellent hydrolysis resistance and making them suitable for applications where water is a consideration [22].

• Polycaprolactone TPUs have the inherent toughness and resistances of polyester-based TPUs combined with low-temperature performance and a relatively high resistance to hydrolysis. They are an ideal raw material for hydraulic and pneumatic seals [23].

TPUs can also be subdivided into aromatic and aliphatic varieties:

• Aromatic TPUs based on isocyanates like MDI that can be used in applications that require flexibility, strength and toughness.

• Aliphatic TPUs based on isocyanates like HMDI, HDI and IPDI are light stable and offer excellent optical clarity. They are commonly employed in automotive interior and exterior applications and as laminating films to bond glass and polycarbonate together in the glazing industry. They are also used in projects where properties like optical clarity, adhesion and surface protection are required [24,25]

2.1.1. Chemistry of thermoplastic polyurethane

A TPU is a multi-phase block copolymer that is created when three basic raw materials are combined with specific way. The components required to produce TPU are:

1. a diisocyanate source: aromatic or aliphatic

2. a polyol: polyester, polyether, polycaprolactone, polybutadiene, castor oil

3. a chain extender: diols or diamines

To prepare an ideal thermoplastic polyurethane, most side reactions should be suppressed. Thus, even traces of water must be avoided [26].

Thermoplastic polyurethane consists of long chain molecules that take conformation of large random coil. These long molecules are soft and flexible at room temperature and they will uncoil when force is applied. The chains are interconnected or cross-linked in ways that allow them to return to their original shape when deforming force is removed. Without inter connectivity property the chain would simply flow when deformed. The polymer chains of thermoplastic polyurethanes have connection by chemical bonds, typical of thermoset materials and physical interactions, typical of thermoplastic materials [27]. The isocynate and chain extender react to form a hard sequence that is commonly referred as ‘hard segment’ and polyol segment is referred as ‘soft segment’. The alternating combinations of hard and soft segments are key feature of thermoplastic polyurethanes from other elastomers shown in (Fig 2.1). Thus, material have such a good properties over wide temperature range [20,28]. In order to obtain ultimate dynamic properties of thermoplastic polyurethane the material needs to be post cured. The most effective post cure temperature is generally just below the melting point of the hard block.

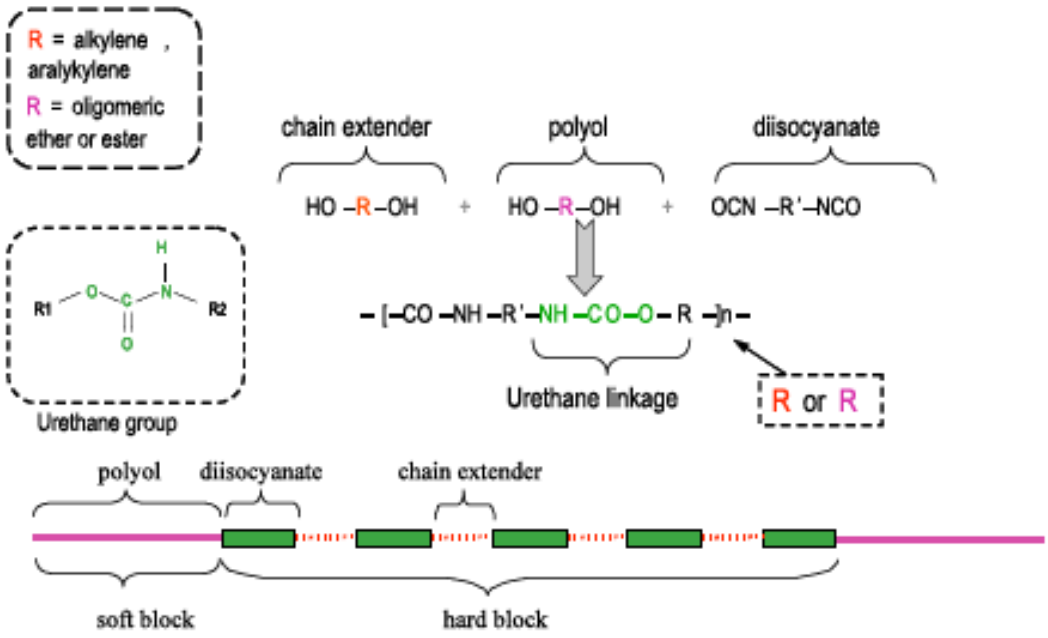

Figure 2.1: Structure of Polyurethane.

The common industrial post cure temperature is 80-120 ^{0}C 15-20 hours. Properties such as resilience, compression set and low temperature can be improved with post cure. These improvements are obtained because there is a reduction in the amount of interphase between the hard and soft segments. Without post cure, the part should be stored for 4 to 6 weeks at temperature above 20 ^{0}C before it is put in service [25,29]. The structures before and after post cure are shown in (Fig 2.2).

2.1.2. Properties of thermoplastic polyurethanes

One of the great challenges of polyurethane chemistry is the almost infinite number of building block combinations. This leads to very different types of TPU, ranging from very soft to very hard, from elastic to rigid and allows very interesting built in properties [30].

2.1.2.1. Elasticity

Elasticity of TPUs are depends on the nature of polyurethane and the molecular weight, the ratio of soft and hard segments, the formulation, the actual temperature, post cure temperature and time.

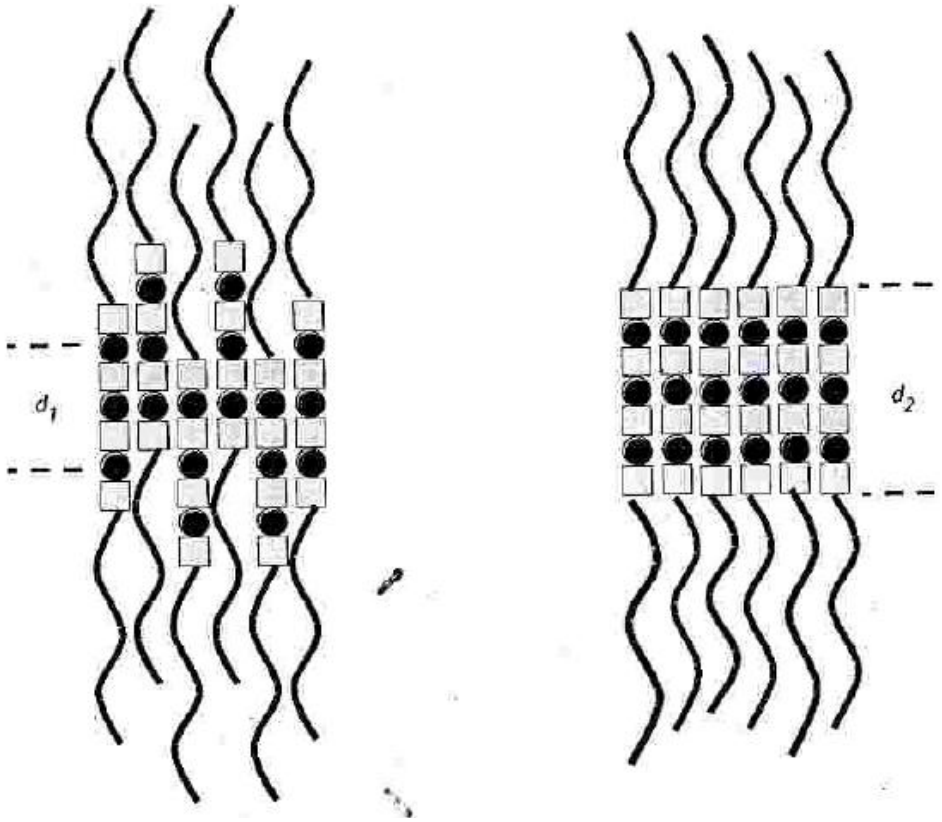

Figure 2.2: Schematic of a hard segment before and after post cure respectively.

2.1.2.2. Thermal behavior

The continuous use temperatures in an unstressed condition are generally estimated at 80 ^{0}C with possible short periods at 120 ^{0}C. A slow thermal degradation can start at 240 ^{0}C with emission of fumes. Service temperatures are lower under loading because of decreasing of modulus. Elongation at break is an especially heat-sensitive characteristic. On the other hand low temperature working condition is promising property of TPUs. The brittle points are generally in the range of -70 ^{0}C up to -65 ^{0}C and TPUs are able to work about -40 ^{0}C.

2.1.2.3. Mechanical properties

The mechanical properties are generally of good to excellent level including abrasion, tear resistance and tensile strength. TPUs have low friction of coefficient. This give them good abrasion and tear resistance. High tensile strength is depending on hard and soft segment lengths and hard/soft segment ratios. Tensile strengths are in the range 20-70 MPa. Post curing improves tensile properties remarkably.

2.1.2.4. Weathering properties

TPU's are generally sensitive to UV and hydrolysis due to their chemistry. Here is a two cases depend on type of hard and soft segment. Firstly, according to soft segment, polyester-based TPU is at risk by hydrolysis when exposed to high temperature levels and in humid environment. Problems typically start to occur when water molecules cause ester groups to split. On the other hand, polyether-based TPU can be used underwater applications as well as humid and damp situations. Secondly, according to hard segment, aromatic-based TPUs can yellow with exposure to UV radiation. In applications where TPU will be exposed to sunlight, choosing aliphatic based will prevent yellowing and degradations.

In addition, usage of stabilizers will improve the TPUs strength against to UV and hydrolysis. Although, weathering conditions are weak point of TPUs, there is lots of alternative combinations to overcome this weakness.

2.1.2.5. Chemical properties

The chemical resistance of TPUs depends on molecular weight, hardness and polyol types. The behavior with pure or salt water at ambient temperature is generally good above 60 ^{0}C. TPUs have good resistance to non-polar fluids, oils and greases. However, strong acids, strong alkalis, aromatics and alcohols quickly attack the polyurethane and contact must be avoided. Dilute acids and bases have a moderate effect at ambient temperature.

2.1.2.6. Flame resistance

TPUs burn inherently easily and are compliant with a UL94 HB rating. FR grades can reach a UL94 VO rating by additional of flame retardant [31-36].

2.1.3. Applications of thermoplastic polyurethane

Thermoplastic polyurethanes have lots of applications due to their unique high tensile strength and elongation, excellent abrasion and tear strength, good resistance to lubricating fluids and fuel oils. Due to these properties, TPUs rapidly became the material of choice for a wide range of critical and can't fail applications. It is not cheap material but its unique properties make it extremely versatile material that performs better than many other thermoplastics. Main applications are automotive,

engineering parts, footwear, medical, pipe, hose and tube, wire and cable, sealing parts.

2.1.3.1. Automotive

TPUs are widely used in automotive due it is its superior properties such as high abrasion resistance, starch resistance, low temperature flexibility, long term stability, high elasticity, high tear resistance pleasant touch and dry feel (Figure 2.3 and 2.4).

Figure 2.3: Gear Knobs and Bearing and Bushes.

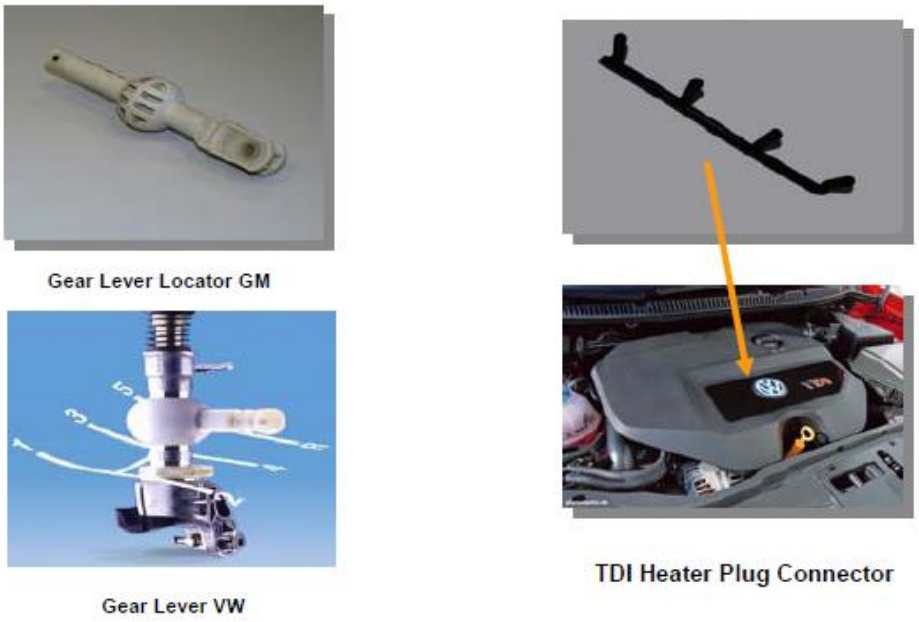

Figure 2.4: Damping Elements and Connectors

2.1.3.2. Engineering Parts

TPUs are widely used for manufacture of gaskets and seals both hydraulic and pneumatic use when wear resistance, rigidity and resistance to oils/greases are essential and polyester-based materials are used. Small and medium sized seals can be produced to a high degree of accuracy by injection molding. Seals can also be directly injected onto metal parts with using metal to polyurethane adhesion promoters. These gaskets and seal are used in construction machines, forklift trucks, lifting platforms, hydraulic presses, injection molding machines, hydraulic cylinders, shock absorbers, car jacks, rotating piston pumps and pneumatic cylinders as a few examples.

Other engineering parts are castor wheels, seals, extruded profiles and mineral classification screens etc (Figure 2.5 and Figure 2.6) [25,27,32,37].

2.1.3.3. Footwear

Footwear is exciting market for TPU due its high usage quantities. TPU exhibits good physical properties, especially including flexibility, durability and abrasion resistance (Figure 2.7) [26, 36].

Figure 2.5: Castor Wheels and Classification Screens.

Figure 2.6: Seals.

2.1.3.4. Medical

TPUs are widely used in medical device industry due to their biocompatibility, excellent physical properties and ease of processibility. It is finding wide application in tubing in medical industry replacing PVC, as its superior properties, such as high burst strength, enable much thinner walled tubes than PVC. Also, the plasticizers in PVC can cause stress cracking in polycarbonate fitting, where TPU doesn't have this problem. The recent studies are available to produce wound dressing with TPU by injection molding [37, 38].

2.1.3.5. Pipe, hose and tube

TPU is preferred in pipe hose and tube industry because of their good hydrolysis and microbial resistance, high burst resistance, excellent abrasion resistance and low temperature resistance [27].

2.1.4. Processing of thermoplastic polyurethane

The ease of processing of the major advantages of TPU. They can be processed by usual melt-processing methods, such as injection molding, extrusion and rotational molding. Some TPUs can be dissolved in solution and they can be processed by the solution production. Each method requires specific grades with suitable melt viscosity and morphology [39].

Figure 2.7: Footwear Applications.

2.1.4.1. Injection molding

Injection molding is a widely used process for the manufacturing of complex products and high production rate. Qualities are generally controlled by process variables such as temperature and pressure. Most grades of TPU can be injection molded. The best processing is achieved by screw pre-plasticization using L/D ratio about 17:1 and compression ratio of between 2:1 and 2.5:1. Temperature control is essential and typical temperature profiles are shown in (Figure 2.8). Typical melt temperatures for different grades are given in (Table 2.1).

Overheating should be avoided, as significant polymer degradation can occur above 230 ^{0}C, but insufficient heating can also lead to degradation due to local overheating from the high shear forces created by processing partially melted material.

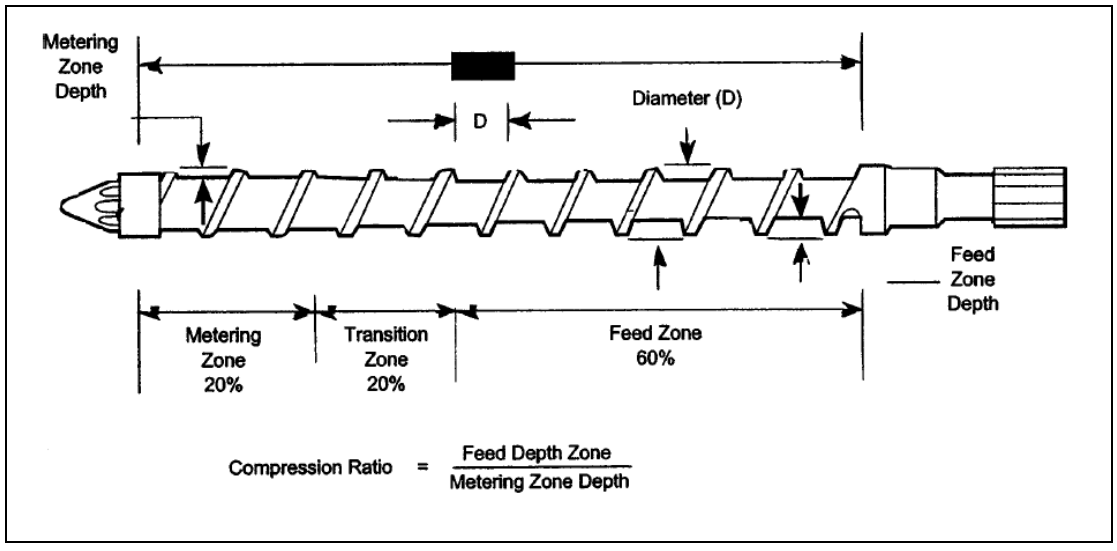

Figure 2.8: Injection Molding Screw of TPU.

Table 2.1: General Melt Temperature of TPU for Injection Molding

Hardness (Shore A)	Hardness (Shore D)	Melt Temperature (^{0}C)
75-90	28-40	180-210
90-95	40-52	190-225
>95	>55	210-245

Polyether-based TPU are more sensitive to overheating than polyester–based TPU. Lower temperatures can be used to help the release thick molding and higher temperatures are sometimes helpful when producing large thin-walled molding such as o-rings and pump diaphragms. TPU molding will shrink by up to 2% from the mould dimensions and the shrinkage can vary with the cross-section of the molding.

Cycle times for a given mould vary with the chemical structure of the TPU and processing conditions. But as general rule caprolactone-based products are faster than polyester-based product, which are faster cycle time than polyether-based products [39-43].

2.1.4.2. Extrusion

Extruder is used for production of compounding, tubes, hoses, profiles, rods and films. TPUs can be extruded with all conventional single and twin screw extruders. TPU can be extruded to produce films sheets, profiles, tubes, hoses, cable sheathing and fibers using there-stage screw with L/D ratios of 24 to 30 and a compression ratio about 3:1. High compression screws cause excessive shear heating and unsuitable. The temperature during extrusion depends on the size of extruder, the output and the grade of the processed material. This vary between 175-230 ^{0}C for TPU. The screw should be driven by oversized, high-torque motor to ensure uniform rotation of screw. The melt viscosity varies with the shear rate and processing controls should include melt pressure and temperature control on the back of the die [39, 44]

2.1.4.3. Rotational molding

Rotational molding is widely used for production of hollow parts usually using polyethylene and PVC compounds. TPU is now competing with PVC as the skin of automotive instrument panels (dashboards). TPU, in the form of powder of micro-pellets, is added the moulds, pretreated with mould-release agent, and moulds are spun with high speed to evenly spread and melt the material. The total cycle time is around three to five minutes dependent on grade of TPU used [25].

2.1.4.4. Powder

TPU can be converted into a powder by cryogenic grinding of the granules or slabs. Powder can be used as holt melt adhesive or can be used for powder plastic blends such as TPU/PVC or TPU/PA alloys [45].

2.2. Polytetrafluoroetheylene (PTFE)

PTFE is a linear chain polymer of straight chain consisting of 20,000-200,000 repeating unit of tetrafluoroethylene (CF4) is shown in (Figure 2.8) [46]. PTFE is a white solid with a waxy appearance and very tough. It is generally considered as a thermoplastic polymer, a very high viscosity at 327 ^{0}C. It can be used itself to produce parts and also can be used as filler for many applications. In contrast to most inorganic functional fillers, PTFE is an organic filler having a unique combination of high thermal, chemical resistance, lowest friction coefficient of any known internal lubricant and high purity. The futures and benefits of PTFE include excellent slip, anti-blocking, improved stability against polishing and improved abrasion, starch and scuff resistance [47].

2.2.1. Types of polytetrafluoroethylene

Commercially, PTFE is produced from the monomer tetrafluoroethylene by two different polymerization techniques. These are emulsion and suspension polymerization. These processes give them vastly different physical forms of chemically identical PTFE is shown (Figure 2.10). While suspension polymerization produces granular PTFE resin, emulsion polymerization produces aqueous PTFE dispersion and PTFE fine powders after coagulating the dispersion.

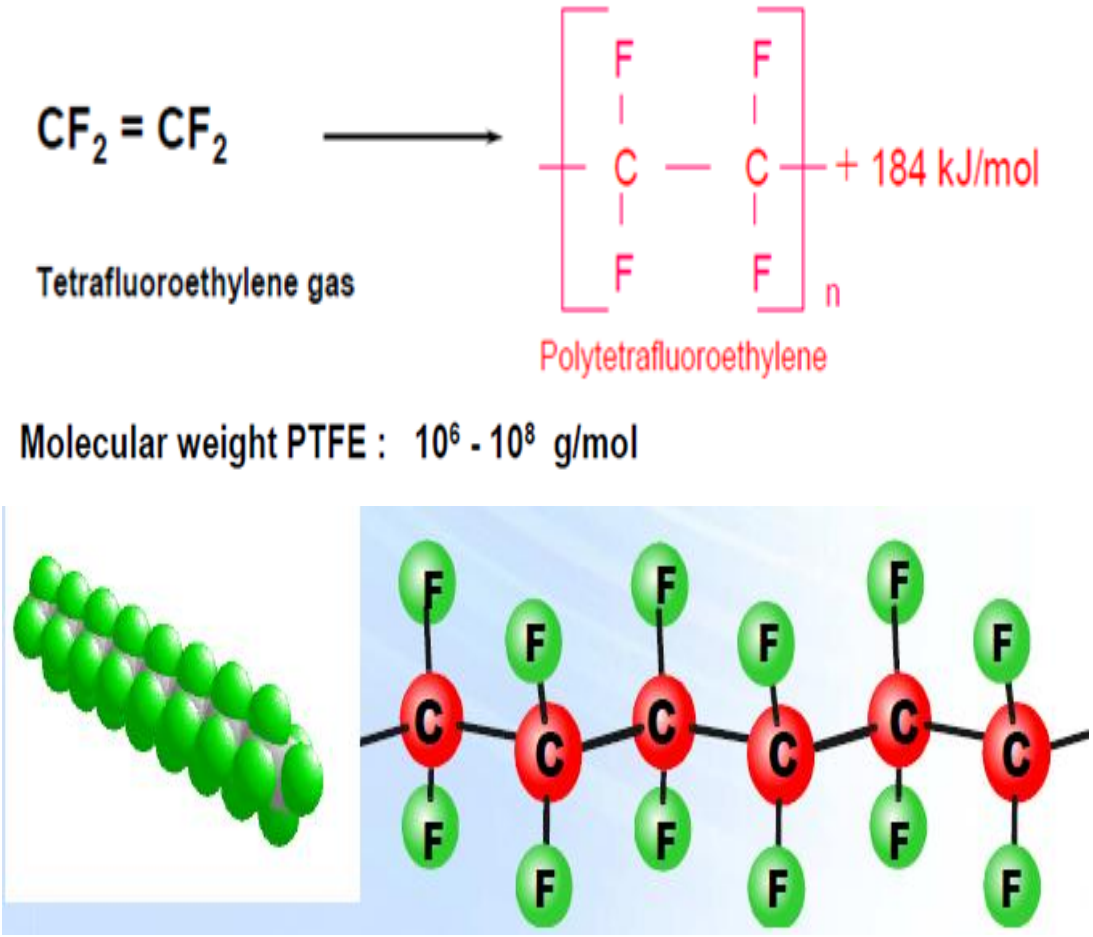

Figure 2.9: Chemical Structure of PTFE.

Micropowders are produced direct polymerization by emulsion polymerization or irradiation of suspension of suspension and emulsion polymerization.

Emulsion polymerization latex has an average particle size of about 150-300 nm. On the other hand, suspension PTFE is produced as reactor bead with dimension of few millimeters. After post treatment and milling, may ground to micron particle size [48-50].

2.2.1.1. Granulars

Granular PTFE is produced by suspension polymerization. Drying and milling is applied to reduce to particle size after polymerization is shown in (Figure 2.11). These particles are about 25µ are not free-flow. Particle size increased to 250-450µ and free flow granular are achieved after re-agglomeration is shown in (Figure 2.12) [51].

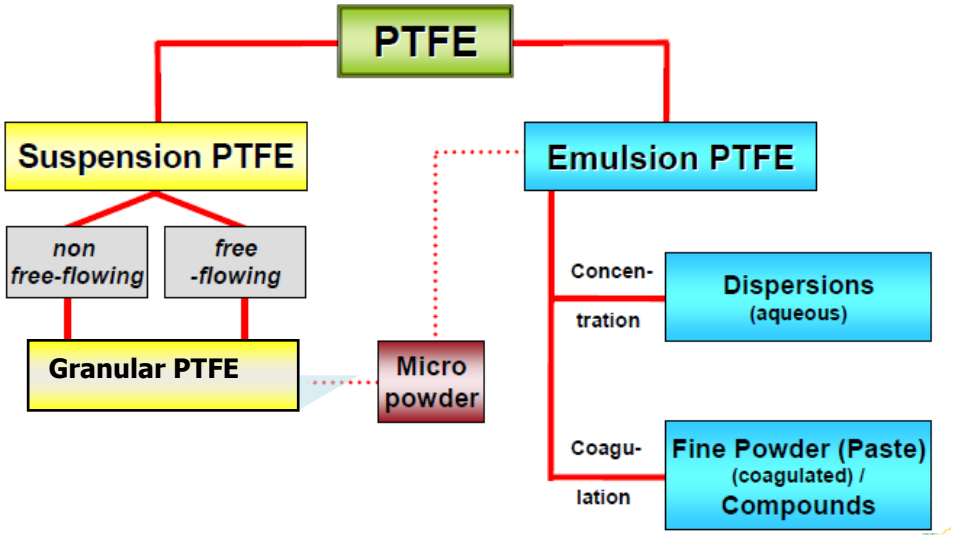

Figure 2.10: Processes of Different Types of PTFEs.

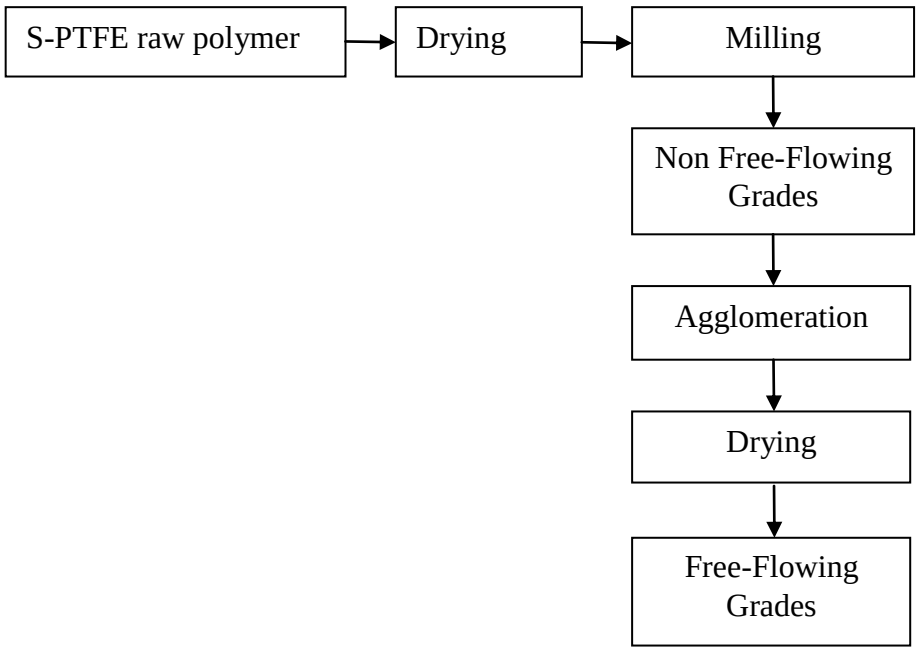

Figure 2.11: Production of PTFE Granules.

Properties of granular PTFE are:

- High density (2,1-2,2 g/cm^3)
- Good tensile strength (20-40 MPa)
- Good elongation at break (250-600 %)

- High contact angle with water (126^{o})
- Very low coefficient of friction (μ : 0,2)
- High melting point range (327 -345 ^{o}C)
- Wide range of service temperature range (-200 ^{o}C to +260 ^{o}C)
- No flammability (V-0, UL94)
- Low permeation to gasses and no water absorption
- Almost universal chemical resistance and insoluble in solvents
- Outstanding light and weathering resistance and no ageing

Type of granular PTFE such as free-flow PTFE is more easy to processed although it has higher particle size than non free-flowing PTFE [6,49,52].

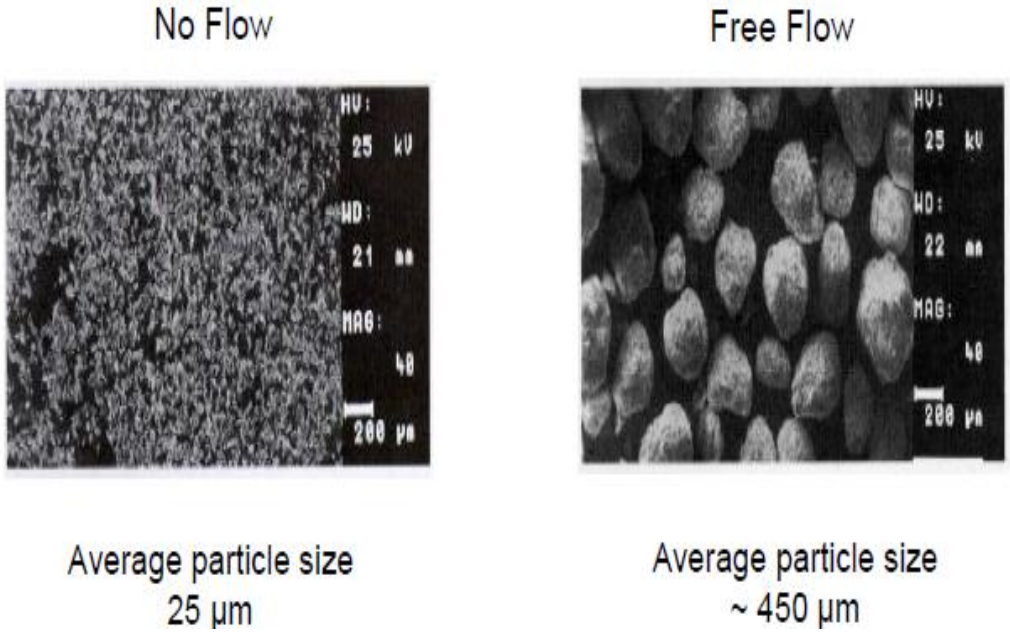

Figure 2.12: Scanning electron microscopy pictures of PTFE granules.

etc. and skieved films, compression molded large sheets, large tubes and cylinders, isostactically molded shapes and sealing is shown (Figure 13) [51].

Figure 2.13: Sealing Production from PTFE Granules.

2.2.1.2. Micropowders

Micropowder PTFE is produced via emulsion polymerization or irradiation of emulsion or suspension polymers. PTFE micropowders are agglomerates or rigid particles

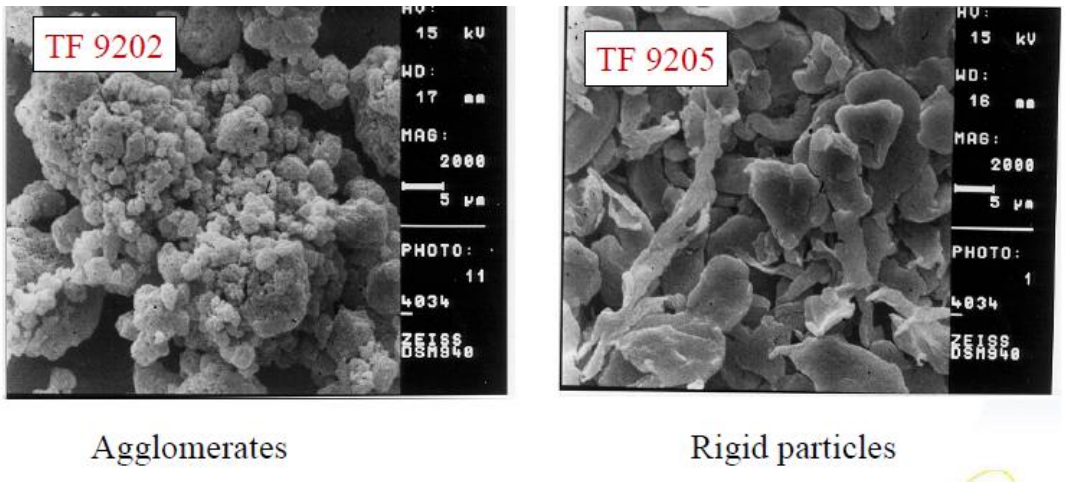

Figure 2.14: SEM pictures of Agglomerates and Rigid Micropowders.

Micropowders having a low molecular weight and show narrow particle size distributions.

Micropowder PTFE has lots of applications mainly as additive due to their superior properties and easy to spread in the carrier systems**.** Applications are :

- Thermoplastics: Micropowder is commonly used in injection moldable thermoplastics such as polycarbonate, polyacetal, polyamide, polyester. It

reduces surface friction and improves sliding properties.hus, it gives better wear resistance to thermoplastics with loading 2,5-20% weight addition

- Elastomers: Micropowder is commonly used in EPDM, NBR, silicone rubber and TPEs. It is added to elastomers during compounding by banbury or two-roll mixer as 10-40% weight. It gives better mold release and wear resistance, reduces surface friction, increase the tear strength and longer the flex life.
- Painting and coating : Micropowder is commonly used in cookware, high quality paint, UV-curable varnish and marine paints. It gives better abrasion resistance, reduced surface stickiness and increased surface hydrophobicity with addition of 2-15% by weight [53-56].

2.2.1.3. Dipersions

Dipersion PTFE is produced by emulsion polymerization tetrafluoroethylene. Dispersions are milky white dispersion of PTFE particles in water and stabilized by wetting agents is shown (Figure 2.15). It has good thermal stability, excellent chemical inertness, good electrical insulating property and low friction coefficient.

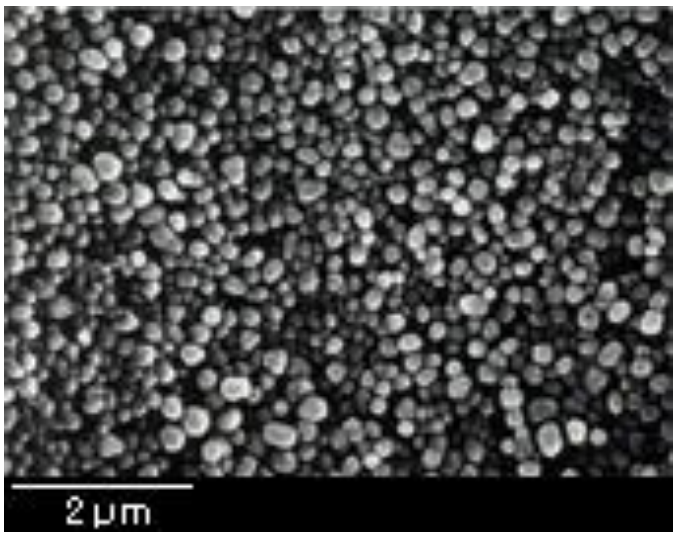

Figure 2.15: PTFE Dispersion (x10.000).

Dispersion has wide applications which are coating of metal such as pans, barbeque, industrials parts and fabric coating of fabrics such as conveyer belt, architecture, backing sheet and impregnation of filter bags, membranes, seals and additive for plastics is shown (Figure 2.16) [53,57-58].

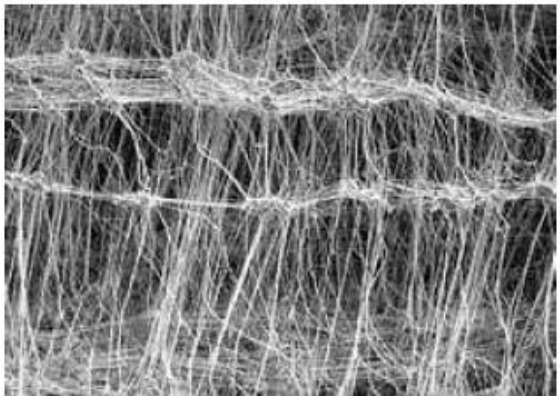

Figure 2.16: Anti-drip Application in Plastics.

2.2.1.4. Fine powders

Fine powder's production starts with emulsion polymerization. After polymerization is completed, raw dispersion of PTFE is coagulated and particle size goes up from 200 nm to 600 μ is shown in (Figure 2.17). The coagulated solution is dried and finally fine powders are achieved.

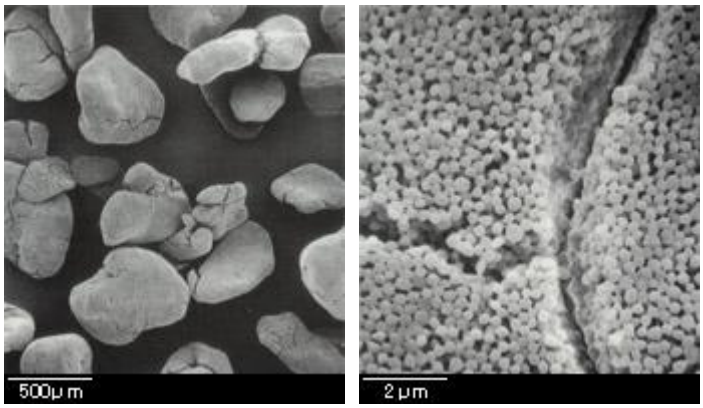

Figure 2.17: Secondary and Primary Particles of Fine Powders

Fine powder is processed by adding lubricants and pastes are produced in this way. Typical applications are wire and cable insulations, tapes, hoses, tubing, profiles, diaphragms and fibers [59-60].

2.3. Polymer blends

Polymer blends is a mixture without chemical bonding that is containing at least two or more polymers. Blend gains properties of each polymers and brings out a new material. Thus, polymer blends have been used to improve the physical and thermal properties of polymer materials in plastic industry [61]. The blend has its own

technical properties, processing conditions and aesthetics. Polymer blend is designed to generate materials with optimized mechanical, structural, morphological and chemical properties. Preparation of individual ratios of polymers, requires many combinations. Polymer blends have become a very important subject for scientific investigation in recent years. Copolymerization and blending are alternative routes for modifications of properties of polymers. Blending is less expensive [62-63].

2.3.1. Polymer blend preparations

Polymer blends are prepared by mixing of polymers. The mixing step is the most important step in the preparation and it is well known that certain properties depend on it [11]. Polymer blends takes 36% of total polymer consumption and their usage is increasing. About 65% of polymer blends and alloys are produced by polymer manufacturers, 25 % by compounding companies and the remaining 10% by transformers. Most common blending methods are heat melting and solution dispersing [10].

2.3.1.1 Heat melting

Heat melting is mixing two or more solid polymers by heating. Screw including melting is used commonly. It supports the heating for better blends. Morphology of blend is strongly influenced by melting and concentration of the each polymers in blend [64]. Differences of the melting or softening point of ingredient show effects on morphology, working temperature and time of mixing. When there is a significant difference in the softening or melting temperatures, it is important to feed polymer to heating zone sequentially. During the heat melting achieved, the polymers have dispersed well. The shear stress is important point during dispersion. Therefore, high speed mixers are not suitable due to cause of high shear during mixing. The mixing should be done in acceptable speed to prevent degradation of polymers. This can be prevented by special machines and screws. The more sophisticated machines and screws is available, the more different polymer blends are able to be produced [65]. The first stages were single screw extruders. Extruders are improved to work on twin screws. Addition to this, with the idea of single screw and more speed of production rate, the injection molding is also used for polymer blends. Studies showed injection molding is also work well as it has single screw behaviors [66].

2.3.1.2. Solution dispersing

The solution dispersion method is mixing of preformed polymer solutions. This is based on a solvent system in which the polymers are soluble. The polymers solutions are mixed well. After required mixing, the solution is poured to mould and solvent is released from the mold. The obtained mold may be final product or be grinded to form granules or dust. This method is mainly used for coatings or small amount of three dimensional parts. It is still poor for high productivity of three dimensional pieces. However, it is still can be used if uniform dispersing is not possible with heat melting [11].

3. EXPERIMENTAL PART

3.1. Materials

There are mainly 2 different materials used in this research. The polymer matrix is thermoplastic polyurethane (TPU). Four different particle size polytetrafluoroethylenes (PTFEs) are used as additive to improve properties of TPU

3.1.1. Thermoplastic polyurethane (TPU)

Elastollan 590 A (BASF) which is polyester based TPU is used as polymer matrix for the preparation of polymer blends. Properties are shown in table 3.1.

Table 3.1 Properties of TPU

Property	**Value**
Hardness (Shore A)	94
Density (g/cm^3)	1,25
Tensile strenth (Mpa)	50
Elongation at break (%)	600

3.1.2. Polytetrafluoroethylene (PTFE)

PTFE powders Dyneon TF 1641, Dyneon TF 1620, Dyneon TF 9205 and Dyneon TF 9202 Z (3M) used for preparation of polymer blends.

Table 3.2 Properties of PTFE powders

	PTFE 450 µ	**PTFE 250 µ**	**PTFE 8 µ**	**PTFE 4 µ**
Property	**Value**			
Avarage particle size (µm)	450	250	8	4
Bulk density (g/l)	830	850	400	300
Specific surface area (m^2/g)			2	11
Melt flow rate MFR(@372 ^{o}C/2.16kg, g/10min)			12	7

3.2. Equipments

3.2.1. Mechanical shaker

Samples are premixed with mechanical shaker SH-100 AVS

3.2.2. Injection molding

Injection molding machine Jon Wai 120 SD with 150 grams barrel capacity is used to prepare blend samples.

3.3. Material Preparation

TPU was dried 4 hours at temperature 110 ^{0}C. Then, dried TPU and PTFE powders were pre-mixed with the mechanical shaker at 50 ^{0}C. Mixtures were fed into the injection molding machine. Blends were produced by injection molding machine. Mixture were molten during plasticizing process at barrel temperature 210 ^{0}C and nozzle temperature 230 ^{0}C. The molten resins were injected to mold pressure at 55 MPa, injection time 12 seconds and screw speed 169 rpm. Blend samples were obtained with dog bone shape mold. Mold temperature was 35 ^{0}C and hold pressure time is 20 seconds. Samples were post cured 20 hours at 90 ^{0}C to get optimum properties of TPU and PTFE blend samples. 7,5% and 10% blend samples also prepared. They were not discussed due to unsuccessful that were taken from TGA analysis. The compositions shown in Table 3.3 were prepared.

Table 3.3: Different compositions of TPU-PTFE blends

Sample code	TPU (%)	PTFE 450 µ (%)	PTFE 250 µ (%)	PTFE 8 µ (%)	PTFE 4 µ (%)
P1-0-0	100	-	-	-	-
P2-450-2.5	97.5	2.5	-	-	-
P3-450-5.0	95	5.0	-	-	-
P4-250-2.5	97.5	-	2.5	-	-
P5-250-5.0	95	-	5.0	-	-
P6-8-2.5	97.5	-	-	2.5	-
P7-8-5.0	95	-	-	5.0	-
P8-4-2.5	97.5	-	-	-	2.5
P9-4-5.0	95	-	-	-	5.0

3.4. Tests and Analyses

3.4.1. Melt flow index test

Melt flow index (MFI) was measured by Tinius Olsen Extrusion Plastomer, MP600 machine followed DIN 1133 at 210 ^{0}C and under 2.16 kg load.

The normalized MFI values calculated by equation given as follows:

$$\text{Normalized MFI: } \frac{\text{MFI of blend}}{\text{MFI of corresponding control unit}}$$

3.4.2. Tensile test

The tensile test was applied to samples for the seeing whether there were effects of PTFE particles on mechanical properties. Samples were produced by injection molding machine. The dimension of samples were 4mm*10mm*168 mm. The samples were tested by U-CAN (Taiwan) tensile machine at 100 mm/min test speed.

3.4.3. Density measurement

Density measurement was used for the first samples and determination of the effect of water test samples. Density of the produced samples were measured by Precisa XB 620 M.

3.3.4. Hardness measurement

Hardness of the samples was determined for the first samples and hydrolysis test samples. Hardness was measured by Vestop (Nishi Tokyo Seimitsu Co. Ltd.)

3.4.5. Contact angle measurement

KSV Cam200 device was used to determine hydrophilicity of the blend. Water was used as wetting liquid and 10 frame/sec is taken under room temperature. The mean value of the first and last frame was taken as contact angle of each sample.

3.4.6. Determination of the effect of the water

The samples were aged by water in Nuve BM 302 machine, under 95 °C and 72 hours with ISO 1817. The samples were taken and tensile tests, hardness and density

measurements were carried out. The differences between aged and un-aged samples were resulted as percentage according to ISO 1817.

3.4.7. Water absorption test

Test was carried out according to ISO D570. Samples were dried 4 hours in oven. First weight was taken and sample were waited in water bath at 25 ^{o}C for 144 hours until they reach the balance. The equation 3.1 was used to calculate water absorption.

$$\text{Water Absorption \%} = 100*(W_2-W_1)/W_1 \quad \textbf{(3.1)}$$

W_1: Dry Sample Weight

W_2: Wet Sample Weight

3.4.8. Abrasion resistance test

Test was done according to ASTM D 1044 named Taber Abrasion. Test was done by Devotrans DA5 D machine. The total path was 40 meters and 10 N abrasion pressure.

The results were followed to determine effects of PTFE powders on abrasion resistance of blends

3.4.9. Thermal gravimetric analysis (TGA)

Perkin Elmer Diamond TGA/DTA was used for TGA analysis. The measurement were done +50 °C to +550 °C with a heating rate of 20 °C /min. The analysis was used to determine the solid content left when the polymer was heated up to 550 °C and determine effect of PTFE on weight loss of TPU.

3.4.10. Differential scanning microscopy (DSC)

Perkin Elmer Diamond DSC was used for DSC analysis. The measurements were according to ISO 11357. The measurement were done -50 to + 250 ^{o}C with a heating rate 20 ^{o}C/min.

3.4.11. Scanning electron microscopy (SEM)

Analysis was use to determine mixture of PTFE powder in TPU matrixes. Scanning electron microscopy, JEOL 5410 was used at 20kV. The samples were coated with gold in order to have conductive samples to measure under SEM and avoid charging.

4. RESULTS AND DISCUSSION

4.1. Mechanical Characterization Results

4.1.1. Melt Flow Index

The effects of the PTFE powders with different particle sizes and varying percentages on the processibility of blends were observed by melt index measurements. The results are shown in Figure 4.1

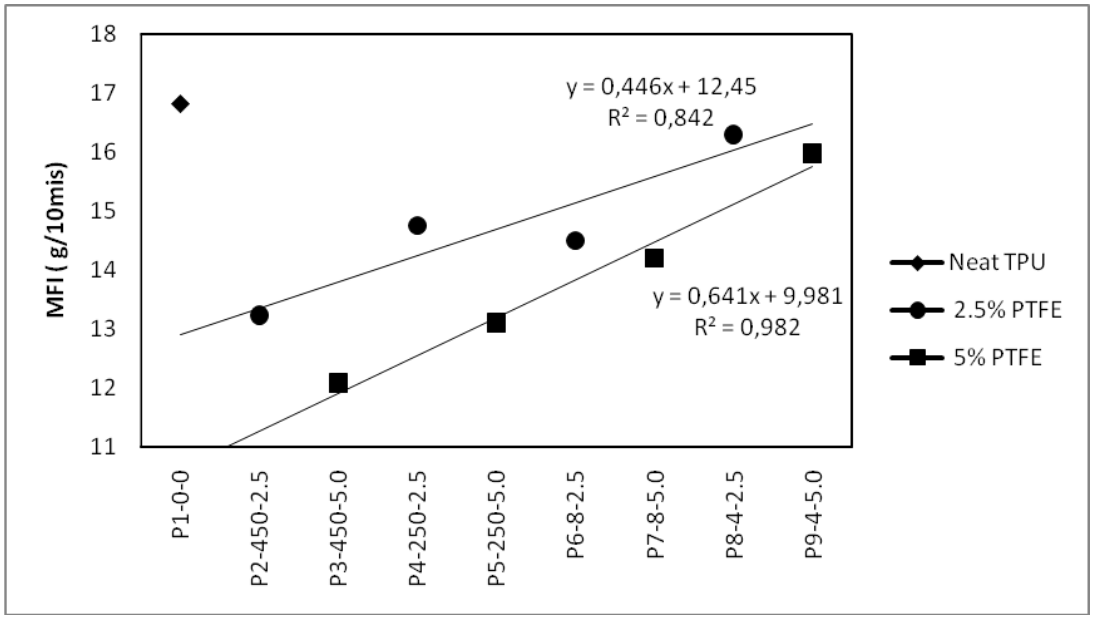

Figure 4.1 MFI Results of TPU/PTFE Blends

Table 4.1 : Normalized MFI Values of TPU/PTFE Blends

Sample code	Normalized MFI (g/10mins)
P1-0-0	1.00±0.000
P2-450-2.5	0.79±0.006
P3-450-5.0	0.71±0.012
P4-250-2.5	0.87±0.014
P5-250-5.0	0.78±0.006
P6-8-2.5	0.86±0.014
P7-8-5.0	0.84±0.013
P8-4-2.5	0.97±0.007
P9-4-5.0	0.94±0.016

The MFI results showed that generally addition of PTFE powders decreased the MFI of the TPU. Decreasing the MFI values with the increase of PTFE amount shows us that PTFE acts as filler in TPU. It is found that, the more small PTFE powders are added to TPU, the less decreasing of MFI is resulted. Result shows that smaller particles are placed in the matrix well and effect less the processibility of TPU than bigger particles.

4.1.2. Density and hardness

Hardness and density results are shown in Table 4.2. The density and hardness increasing were expected with addition PTFE powders to TPU due higher density

and hardness of PTFE. Increasing in density can be seen easily. However, increasing in hardness is small amount and does not show regular changing.

Table 4.2 Hardness and Density of TPU/PTFE Blends

Sample code	Hardness (ShA)	Density (g/cm^3)
P1-0-0	90	1.251
P2-450-2.5	92	1.282
P3-450-5.0	91	1.307
P4-250-2.5	91	1.270
P5-250-5.0	92	1.281
P6-8-2.5	91	1.264
P7-8-5.0	92	1.280
P8-4-2.5	91	1.261
P9-4-5.0	92	1.277

4.1.3. Tensile results

The results of the tensile test are given Figure 4.2

As shown that the mechanical properties of TPU-PTFE blends are similar to neat TPU until 300% strain. This shows that blends can act as neat resin without changing of properties until 300% strain. However, decreasing is seen with increasing the amount of PTFE powder in each blend at strength at break. This behavior is reverse effect of MFI values.

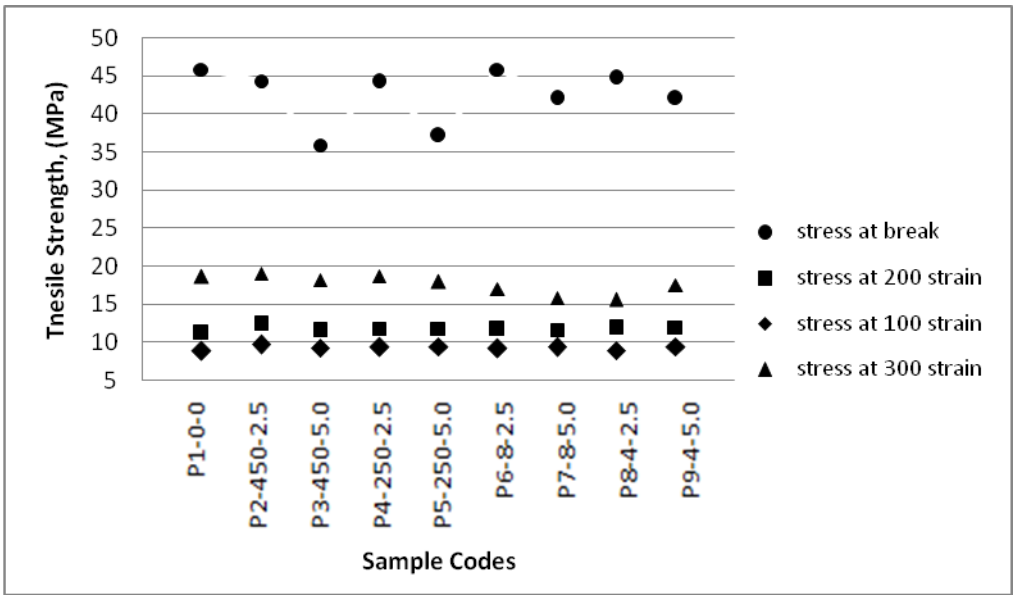

Figure 4.2: The mechanical properties of the TPU and TPU-PTFE blends

This shows us that, the reduction in tensile strength may be due to reduction in intermolecular attraction between the polyurethane chains. Because, PTFE may act as inert filler and which may break the intermolecular bond and reduces the cohesive strength with its lubricating property. This effect is not big until 300% strain. However, bigger effect can be seen clearly at strain at break.

There is several theories of the dependence of blend properties on filler-volume fraction "Φ" and geometry have been investigated, in a simple model Nicolais and Narkis. They developed a geometrical model for tensile strength "σ" of a blend with uniformly distributed spherical filler particles of equal radius is shown in equation 4.1.

$$\sigma_b = \sigma_0(1-K\Phi^{2/3}) \qquad \textbf{(4.1)}$$

The subscripts "b" and "o" represent the blend and the matrix respectively. "K" value of 1.21 is no adhesion of filler and matrix [67-70]. The calculated and experimental tensile strength at break is shown in Figure 4.3 and K values are given in Table 4.3. As shown in Figure 4.3, the behavior of experimental results are similar to theoretical calculation results. From Figure 4.3, the smaller particles we have in blend, the less changing occurs according to neat TPU in TPU/PTFE blends.

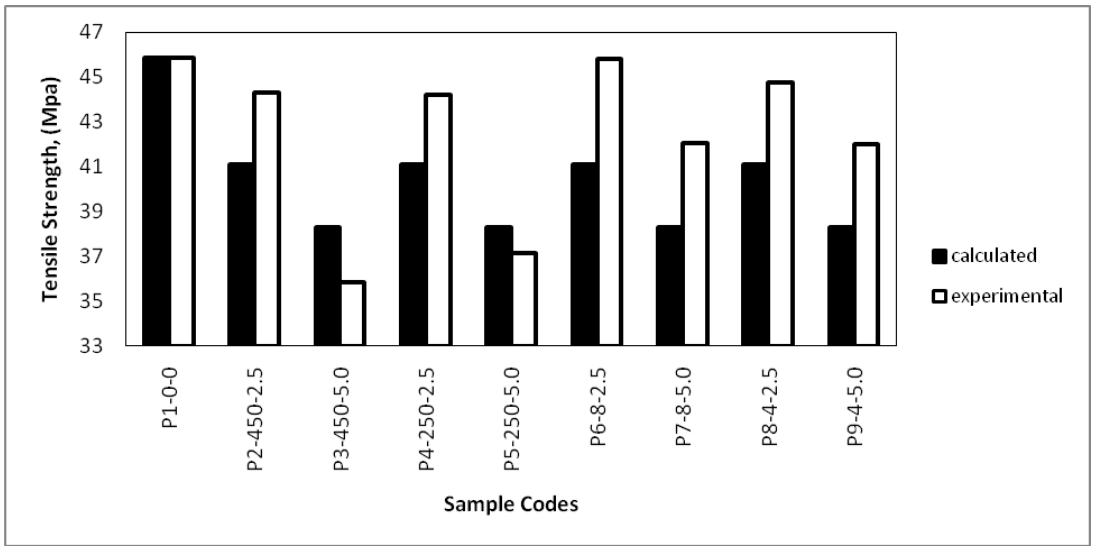

Figure 4.3 : Calculated and experimental tensile strength results

Table 4.3 K values of polymer blends

Sample code	**K value**
P1-0-0	0±0.0
P2-450-2.5	0.40±0.42
P3-450-5.0	1.39±0.01
P4-250-2.5	0.38±0.01
P5-250-5.0	1,60±1.08
P6-8-2.5	0.01±0.01
P7-8-5.0	0.60±0.15
P8-4-2.5	0.26±0.20
P9-4-5.0	0.61±0.21

Additionally, blends including small particles are above the theoretical graphic at 5% concentrations at large particles are below the graph. This is supported in Table 4.3 that small particles are always have K value less than 1.2 that indicates better bonding. Large PTFE particles are affected negatively from the increasing amount of PTFE at 5%. This may be the reason of breaking of TPU chains by the larger particle size PTFE powders. The high deviation at sample P3-450-5.0 is noticed and may be caused by break of large particles due to shear stresses. The values on the Figure 4.3 indicate that, samples on the theoretical values from the graph have no adhesion of PTFE powders with TPU matrix at samples and samples above the theoretical values have adhesion of PTFE powders with TPU matrix.

4.1.4. Water absorpsiton

From the Figure 4.4, all PTFE/TPU blends are less tendency to get water in their matrix than neat TPU. This shows the hydrophobic property of PTFE particals in the TPU matrix. The best samples are P5-250-2.5 and P9-4-5.0 according to the test results

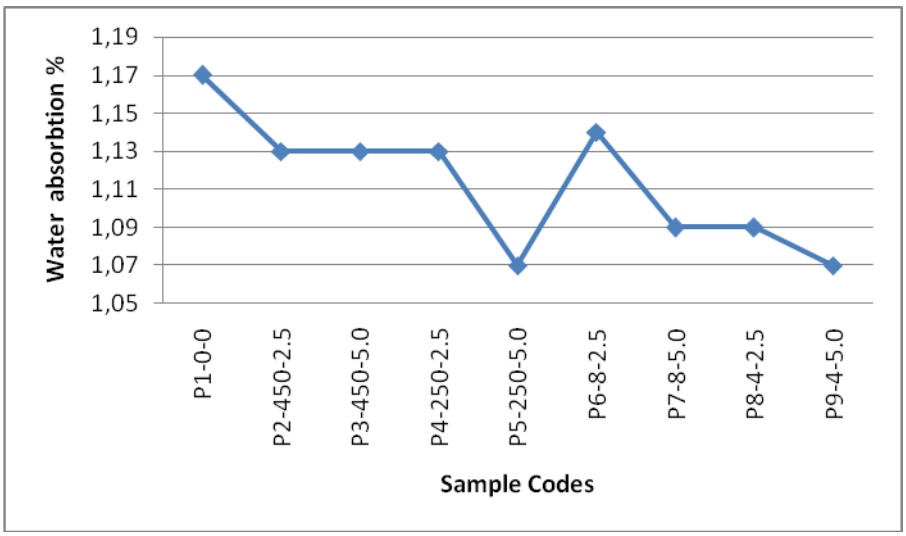

Figure 4.4: Water absorption of blend samples

4.1.5 Contact angle

From Figure 4.5, TPU is hydrophilic and addition of all level and particle size of PTFE increases its hydrophobic behavior.

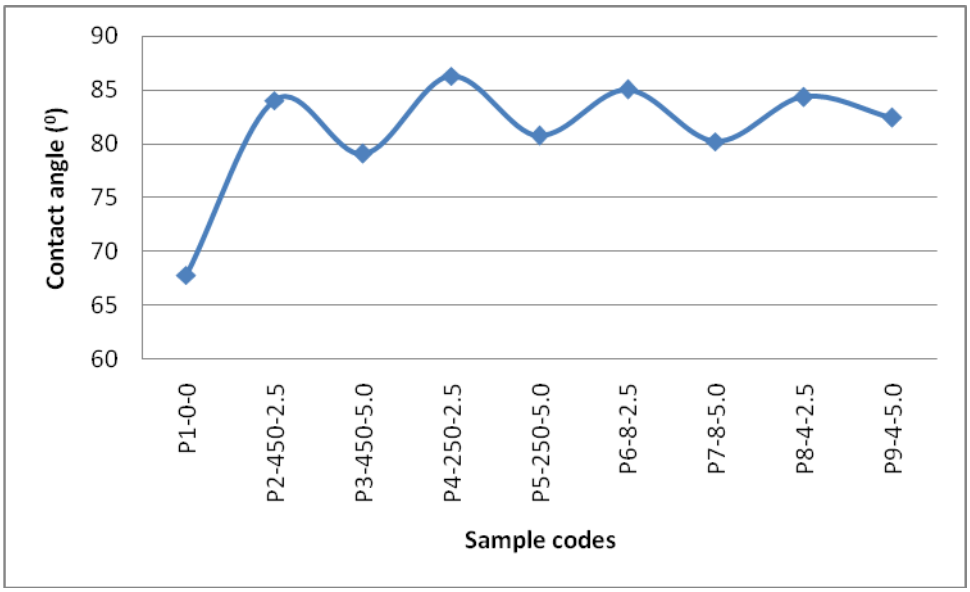

Figure 4.5 Contact angles of polymer blends

From the graphic, there is decreasing with increasing the amount of each particle size PTFE powder. There is interestingly, there is almost same difference between 2.5% and 5.0% concentrations with decreasing of particle size. This may be the reason of decreasing the adhesion of PTFE particles to TPU matrix affects the morphology.

4.1.6. Determination of the effect of the water

Results are shown in Table 4.4 that the stress, hardness and density are decreasing and elongation is increasing for all samples.

Table 4.4 Effects of water on the polymer blends.

Sample codes	Differences in tensile strength at break %	Differences in elongation at break %	Differences in hardness %	Differences in density %
P1-0-0	-17.78	35.30	4.44	4.44
P2-450-2.5	-19.89	16.74	2.20	0.71
P3-450-5.0	-11.51	43.31	0.00	0.62
P4-250-2.5	-4.23	44.18	0.00	1.55
P5-250-5.0	-11.71	38.28	2.17	0.62
P6-8-2.5	-4.58	33.28	3.30	3.30
P7-8-5.0	-4.97	-7.54	2.17	2.17
P8-4-2.5	-19.61	1.96	2.20	2.20
P9-4-5.0	-10.92	9.72	2.17	2.17

This shows that TPU is absorbing water inside and decreasing its mechanical properties during aging. PTFE powder added samples are in better conditon according to neat TPU are from the overall results, sample P7-8-5.0 shows significant resistance to aging. Sample P9-4-5.0. From the test results, the smaller particles have better resistance than larger particles in water aging. This may be reason of beter adhesion of small PTFE particles to TPU matrix than larger PTFE particles.

4.1.7. Abrasion resistance

The well known friction decreasing property of PTFE can be seen easly in all blends according to abrasion test results. Although, all blends samples show better result than neat TPU, small PTFE powders are all better abrasion resistance than large

PTFE powder. The samples P7-8-5.0 and P8-4-2.5 are the best two of all samples in abrasion test.

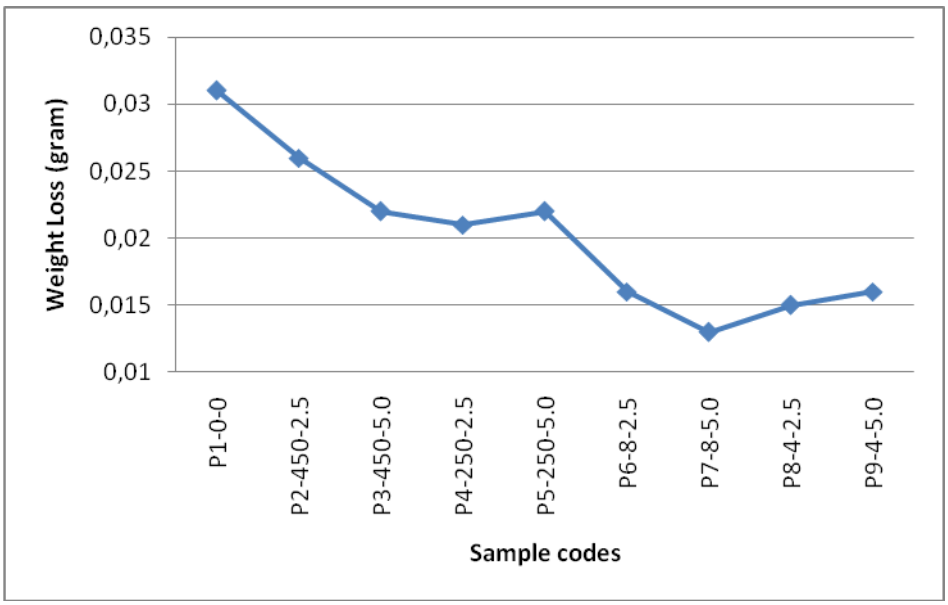

Figure 4.6: Abrasion resistance test results

4.2. Thermal properties result

4.2.1. TGA

From Table 4.5, the PTFE concentration of the polymer blends were seen.

Table 4.5 PTFE concentration of polymer blends.

Sample code	PTFE weight @ 550 °C (%)
P1-0-0	0,00
P2-450-2.5	3.04±0.16
P3-450-5.0	4.27±0.36
P4-250-2.5	2.48±0.38
P5-250-5.0	4.47±0.04
P6-8-2.5	2.53±0.38
P7-8-5.0	5.26±0.22
P8-4-2.5	2.29±0.01
P9-4-5.0	5.25±0.28

4.2.2 DSC

Effect of PTFE on Tg values were investigated by DSC. From Table 4.6, there is no significant changing on Tg due to low amount addition of PTFE

Table 4.6 Tg values of polymer blends.

Sample code	Tg/ ^{o}C
P1-0-0	-16.87±1.68
P2-450-2.5	-17.27±0.68
P3-450-5.0	-16.88±0.15
P4-250-2.5	-16.435±1.52
P5-250-5.0	-16.66±0.99
P6-8-2.5	-18.13±0.11
P7-8-5.0	-15.6±1.48
P8-4-2.5	-17.81±1.30
P9-4-5.0	-15.71±1.67

4.3. SEM

Samples P5-250-5.0 as large and P7-8-5.0 as small particle were investigated with SEM. Since TPU is soft thermoplastic and low Tg around -50 ^{o}C, the samples couldnt break just with liquid nitrogen. The TPU based blends can be broken SEM investiogations in liquid nitrogen and than stained with RuO_4 [71]. Due to unavilablity of materials, SEM samples were cutted with sample cutting device and morphlogy should be damaged.

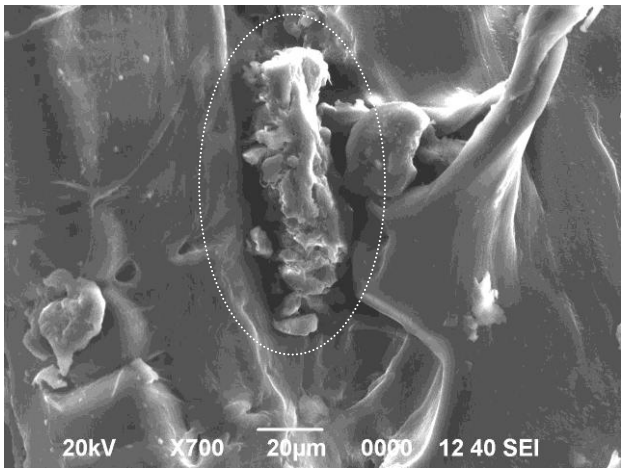

Figure 4.7. SEM micrographs of Sample P5-250-5.0

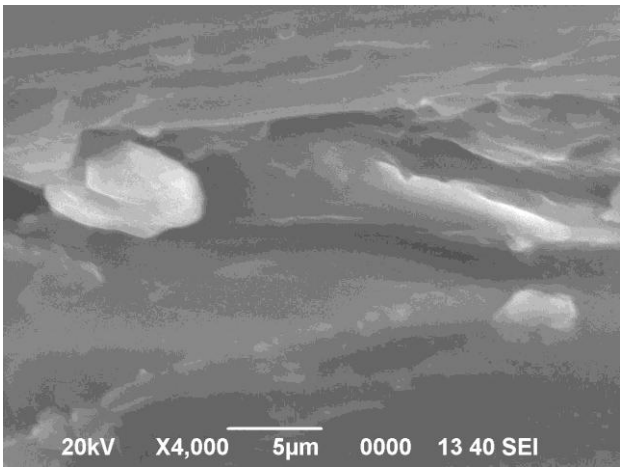

Figure 4.8 SEM micrographs of Sample P7-8-5.0

From Figure 4.7, large PTFE particles may faced with shape changing due to shear stress. Therefore, the blends were not good enough. From Figure 4.8, small particles are spread well in the matrix and bond well with the matrix.

5. CONCLUSION

The aim of this study was to enhance the properties of thermoplastic polyurethane (TPU) by blending with polytetrafluoroethylene (PTFE). There were used 4 different particle size to see effects of particle size of PTFE in TPU blends. Samples were tested abrasion resistance, tensile strength and effects of water.

The results showed that, addition of PTFE up to 5% to TPU increased the properties of blending such as abrasion, water absorption and decreased the effect of water under working condition. The small particles spread in the TPU matrix better than large PTFE particles. Especially, small particles showed better properties in mixing and better properties than larger particles in abrasion resistance and effects of water. Although, all TPU/PTFE blends were better than neat TPU in abrasion test, maximum 2.38 times more abrasion resistance was developed which at sample P7-8-5.0. The tensile tests after ISO 1817 test showed good resistance could achieved with samples P6-8-2.5 and P7-8-5.0

Slight changing is tensile properties until 300% strain is encouraging result that TPU/PTFE may still keep its elastic properties under working condition.

This study is able to be applied for sealing and castor wheels and where the abrasion and water is the obstacle for TPU.

The further studies can be done for small size PTFE powders with twin screw extruders to see differences between injection molding blending and twin screw extruder blending of TPU and PTFE.

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APPENDICES

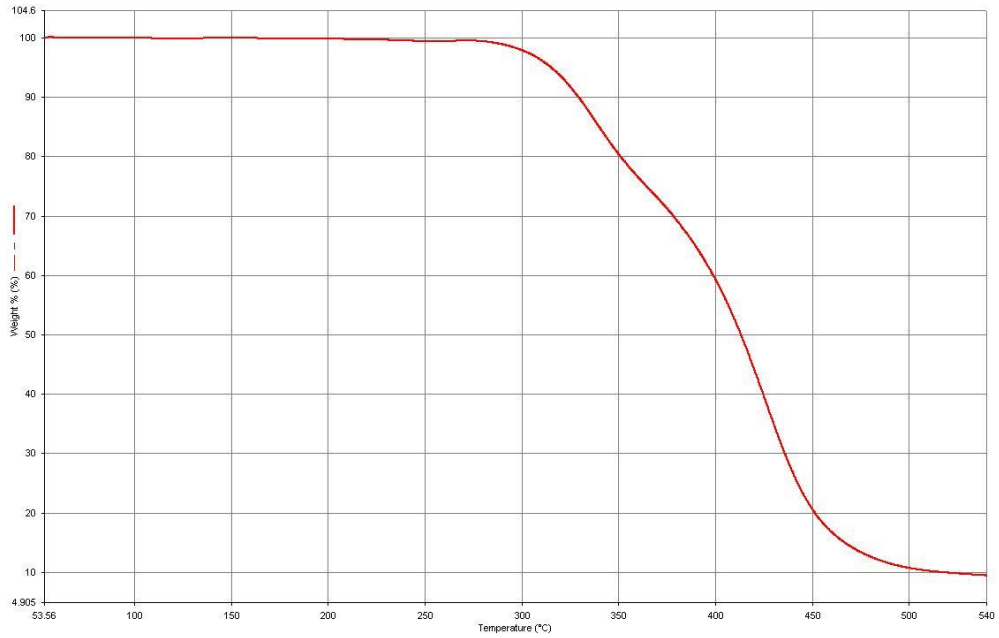

Figure A.1 : TGA of Sample P1-0-0

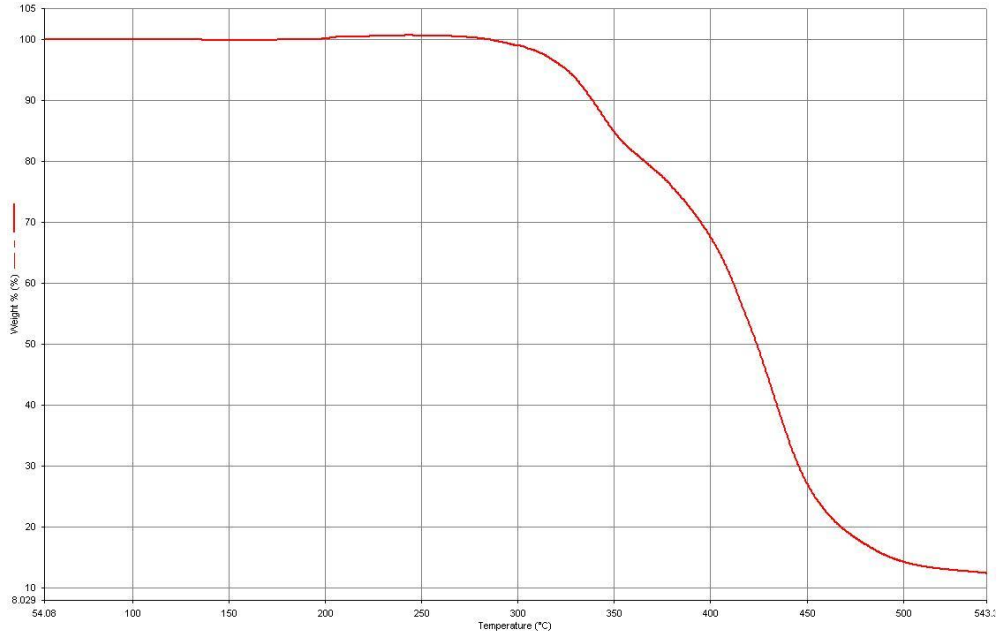

Figure A.2 : TGA of Sample P2-450-2.5

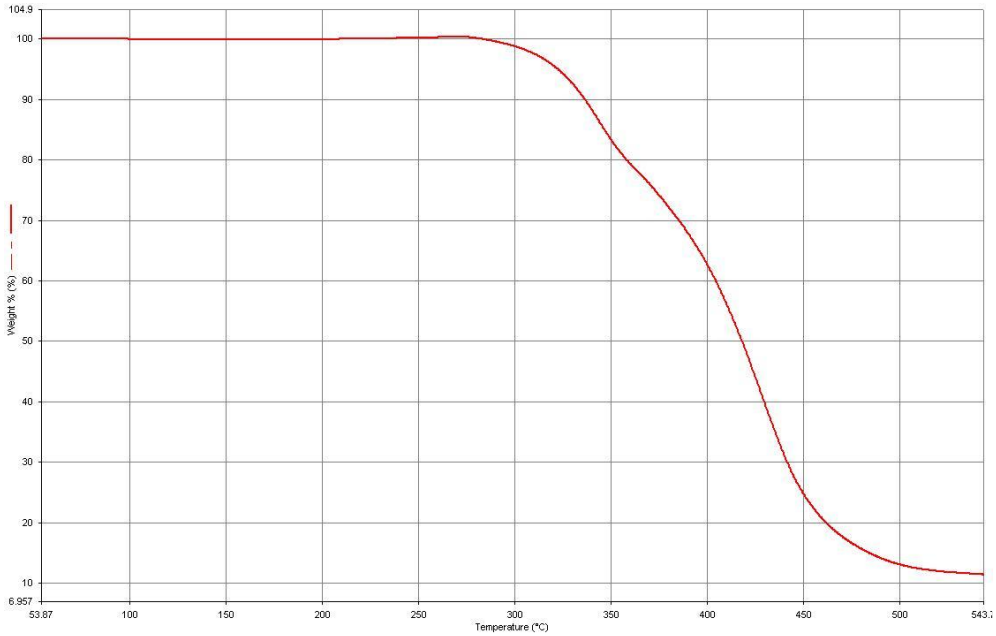

Figure A.3 : TGA of Sample P3-450-5.0

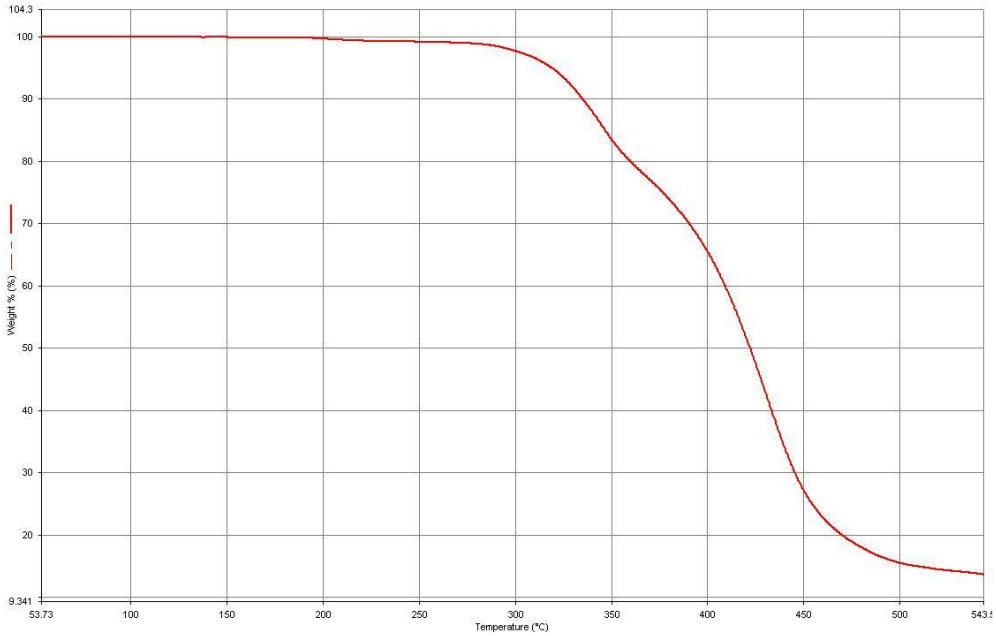

Figure A.4 : TGA of Sample P4-250-2.5

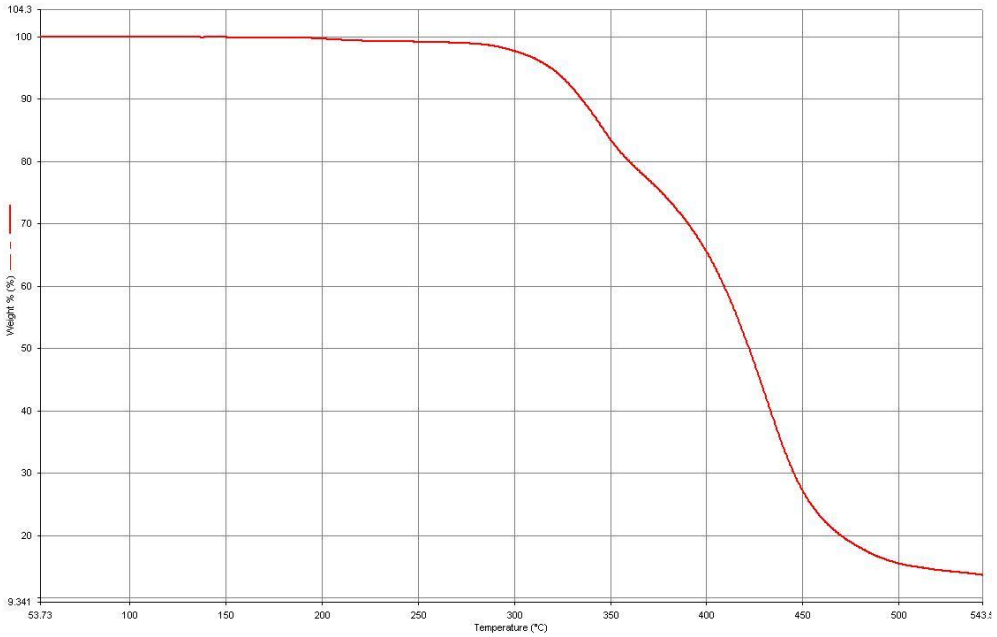

Figure A.5 : TGA of Sample P5-250-5.0

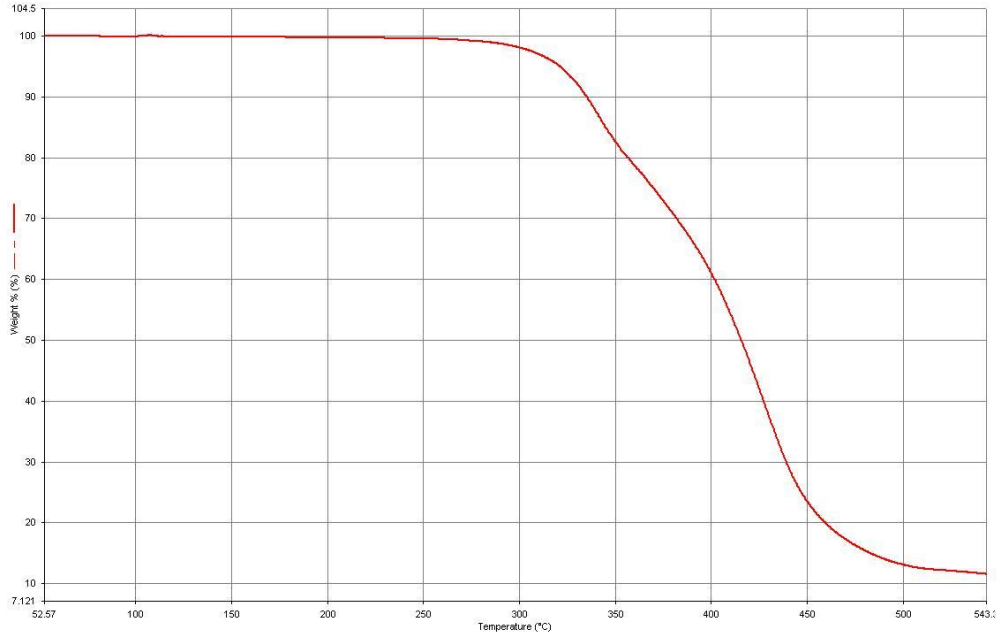

Figure A.6 : TGA of Sample P6-8-2.5

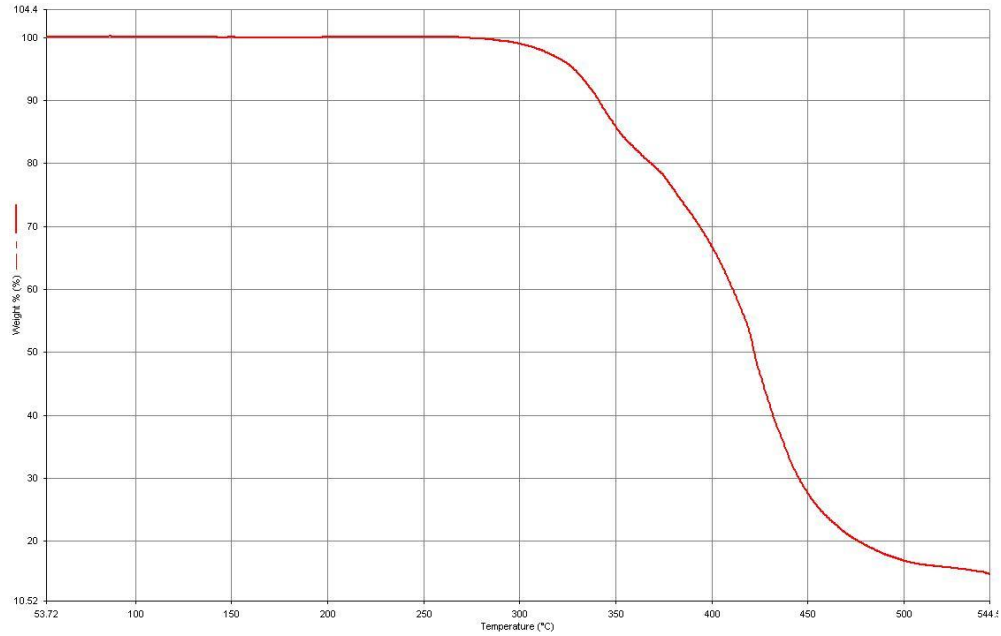

Figure A.7 : TGA of Sample P7-8-5.0

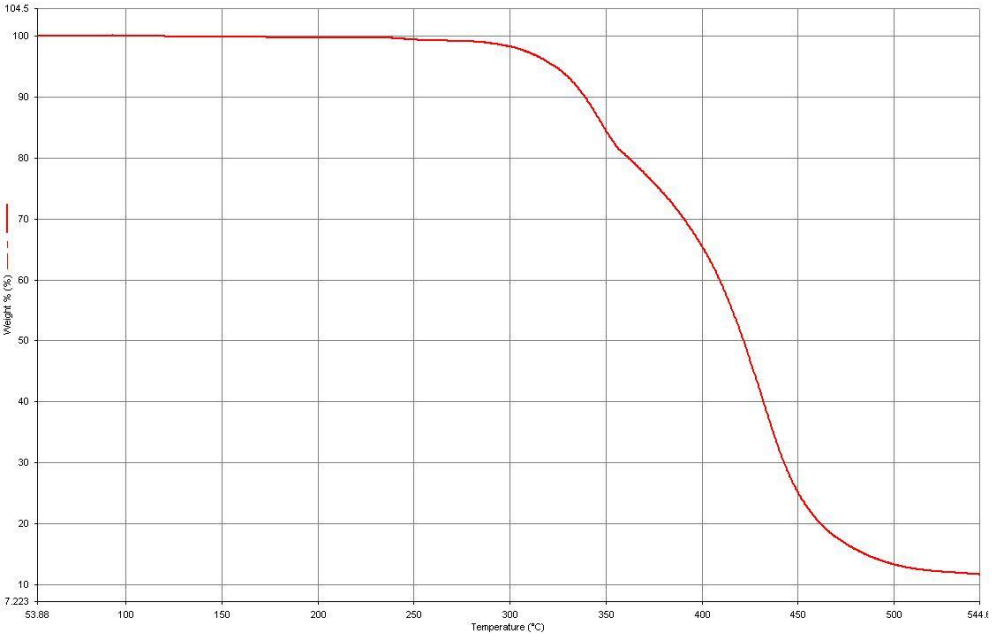

Figure A.8 : TGA of Sample P8-4-2.5

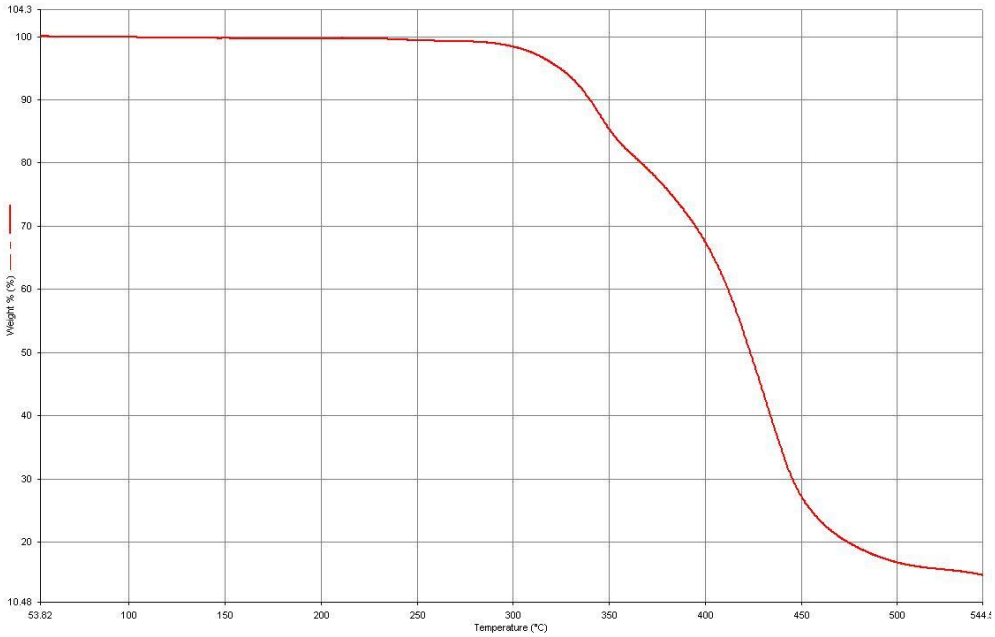

Figure A.9 : TGA of Sample P9-4-5.0

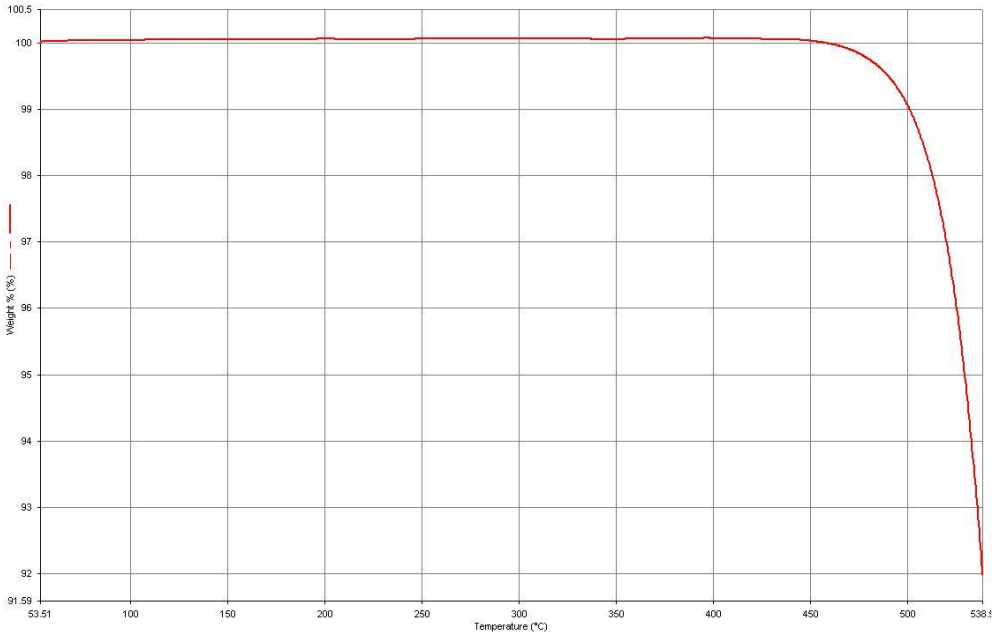

Figure A.10 : TGA of PTFE 450µ

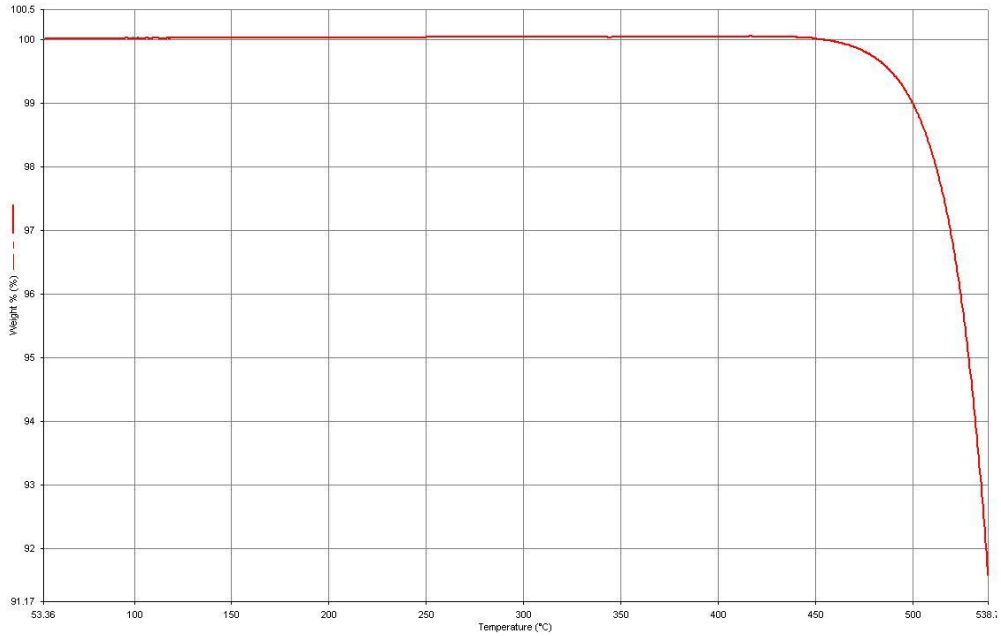

Figure A.11 : TGA of PTFE 250µ

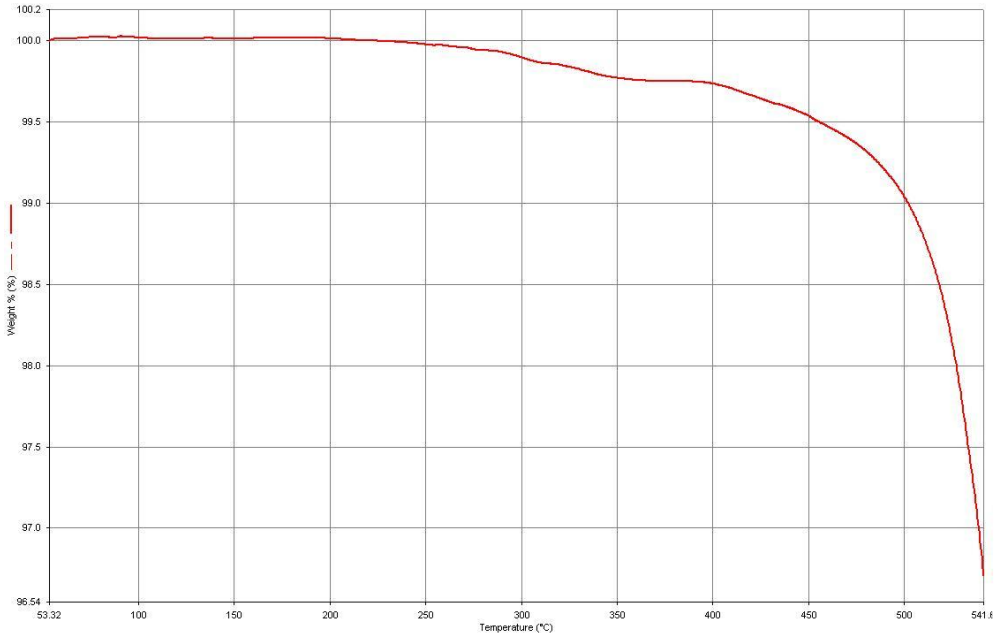

Figure A.12 : TGA of PTFE 8µ

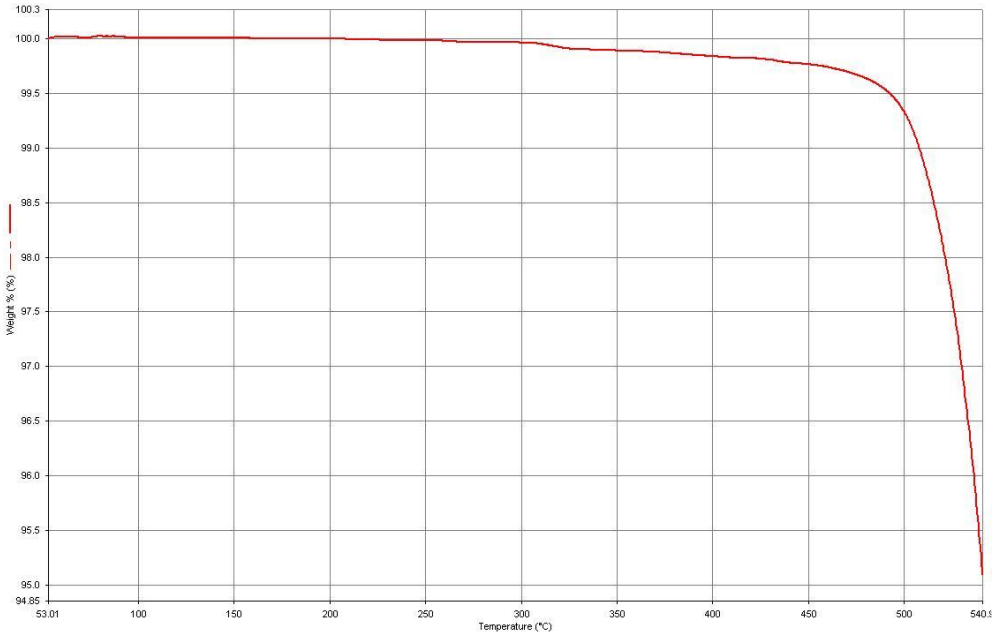

Figure A.13 : TGA of PTFE 4µ

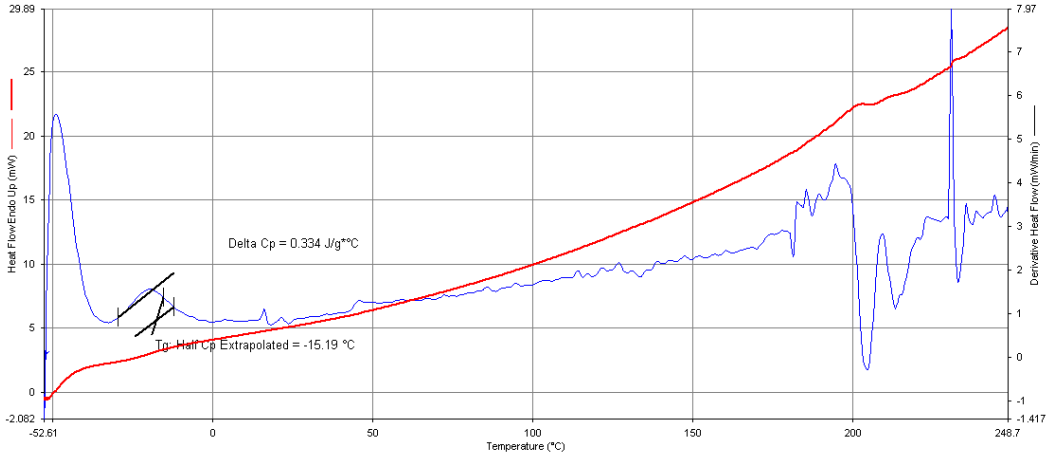

Figure B.1 : DSC of Sample P1-0-0

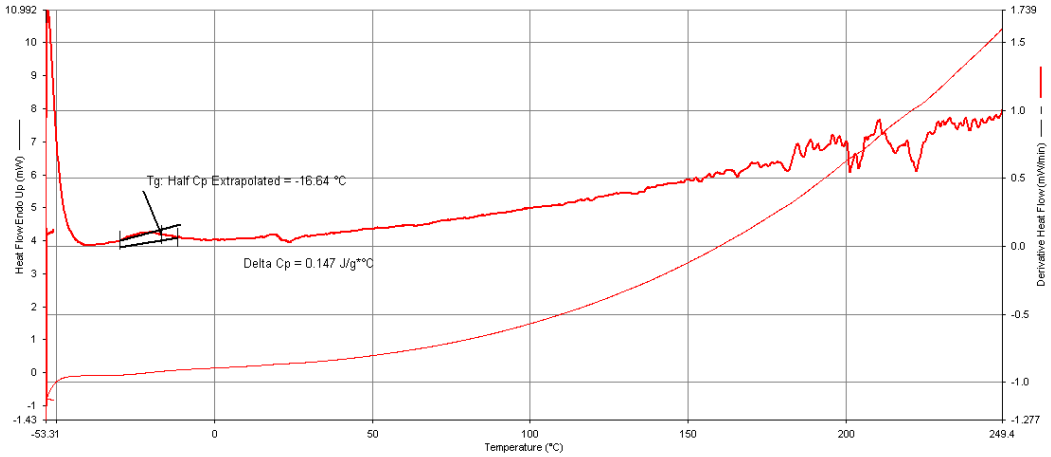

Figure B.2 : DSC of Sample P2-450-2.5

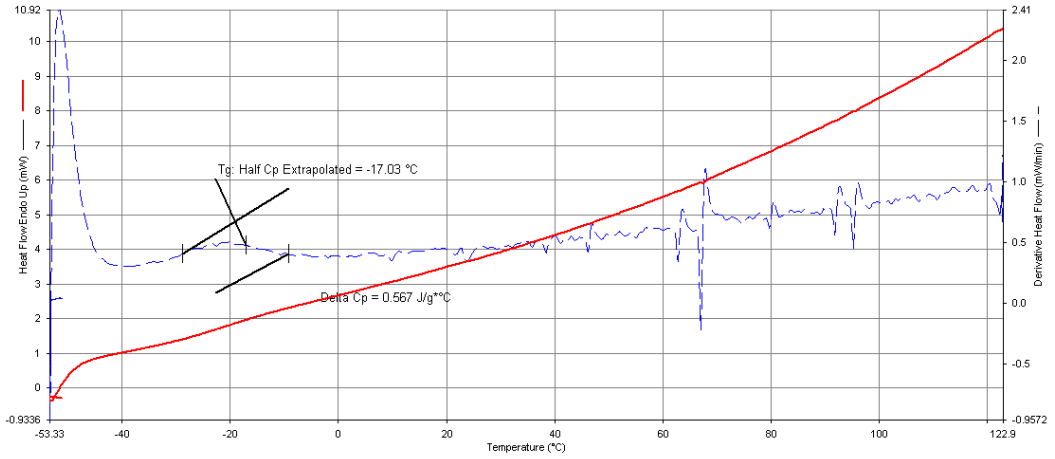

Figure B.3 : DSC of Sample P3-450-5.0

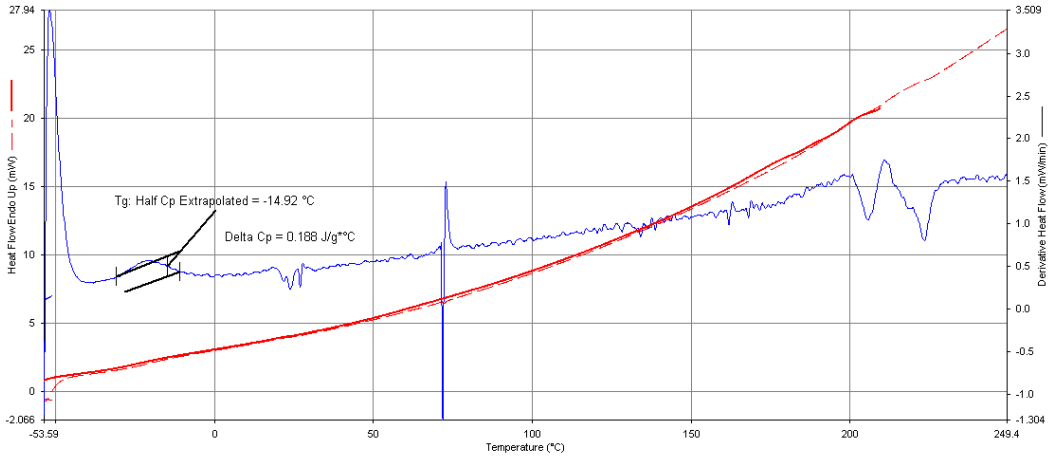

Figure B.4 : DSC of Sample P4-250-2.5

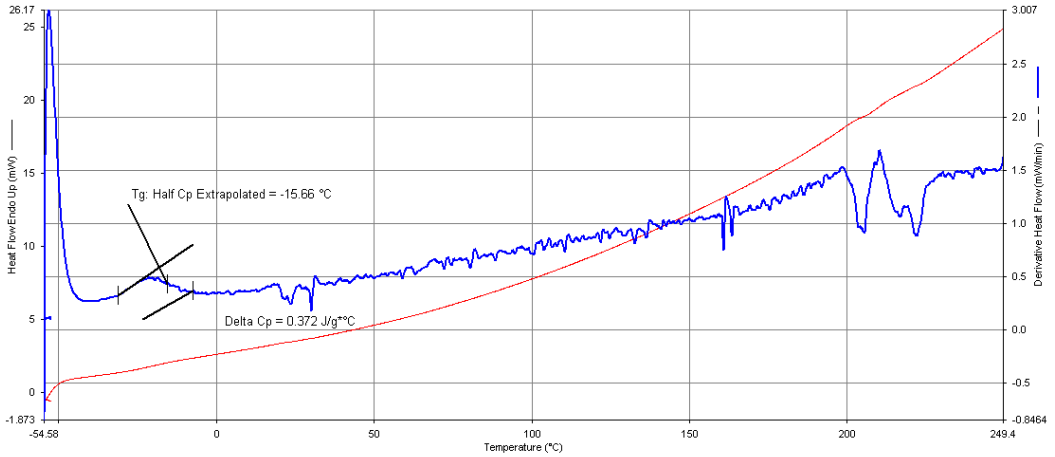

Figure B.5 : DSC of Sample P5-250-5.0

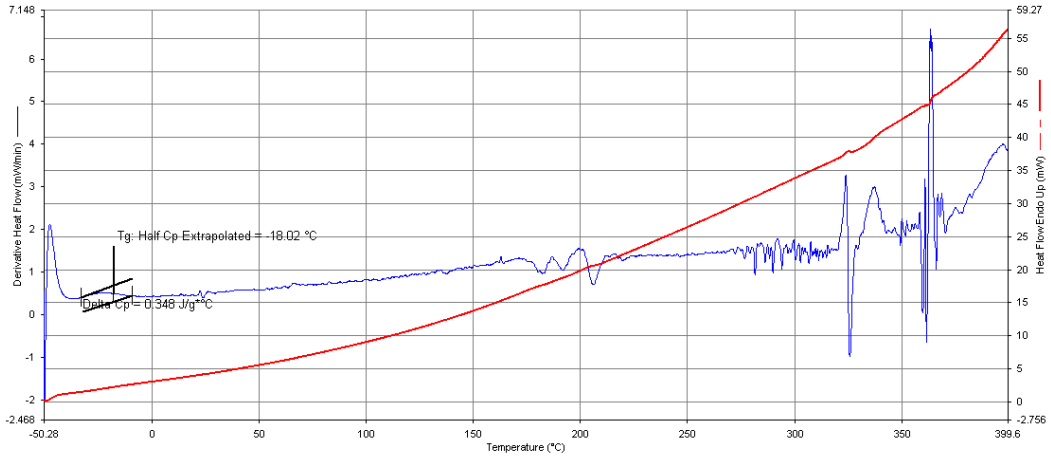

Figure B.6 : DSC of Sample P6-8-2.5

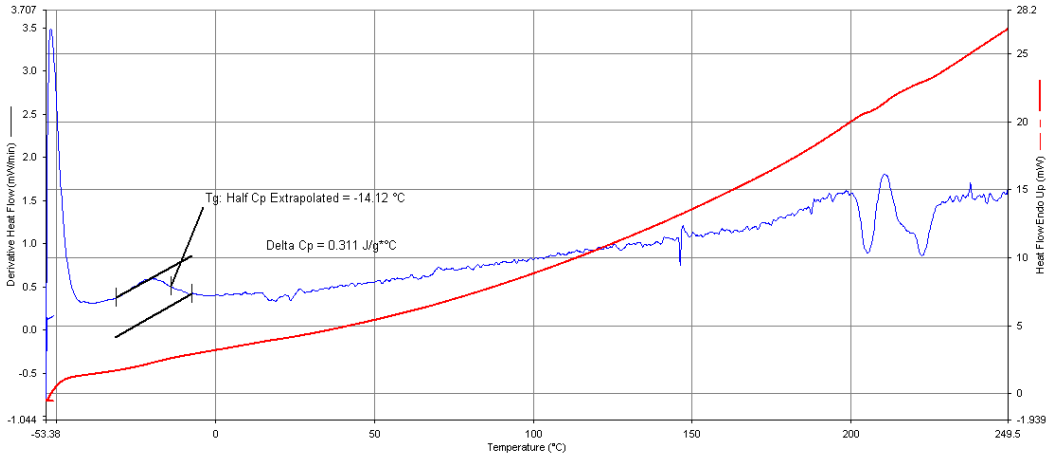

Figure B.7 : DSC of Sample P7-8-5.0

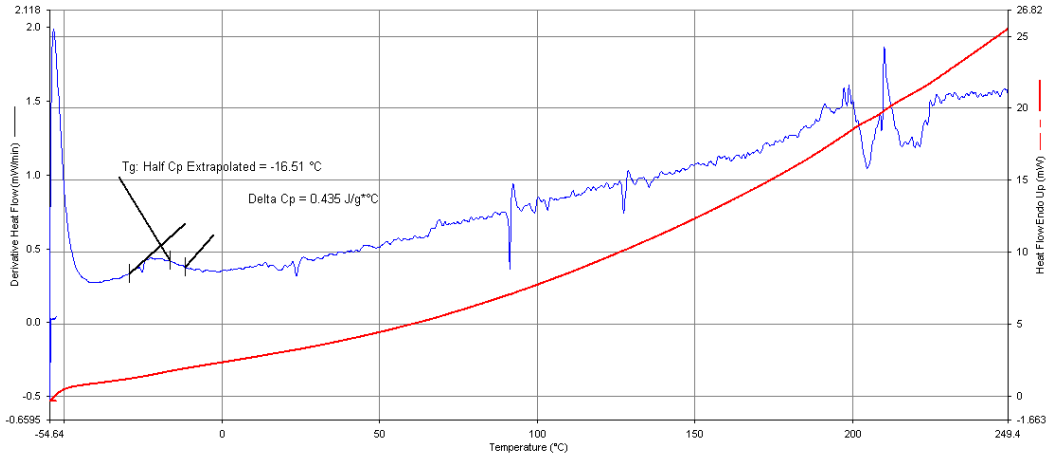

Figure B.8 : DSC of Sample P6-4-2.5

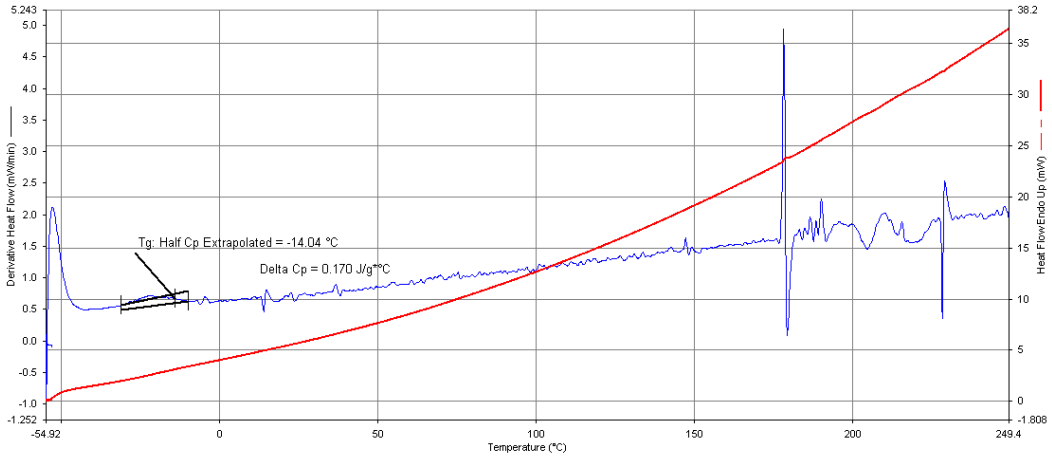

Figure B.9 : DSC of Sample P9-4-5.0

Table A.1: Stress at Break Values of Blend Samples

Sample code	Stress at Break 1st Values (N/mm2)	Stress at Break 2nd Values (N/mm2)
P1-0-0	45,83	45,75
P2-450-2.5	44,32	45,83
P3-450-5.0	35,855	37,15
P4-250-2.5	44,225	44,32
P5-250-5.0	37,15	29,14
P6-8-2.5	45,82	45,8
P7-8-5.0	42,06	41,08
P8-4-2.5	44,77	43,93
P9-4-5.0	42,02	40,68

Table A.2: Stress Values of Blend Samples at Different Strains

Sample code	Stress at 100 Strain (N/mm2)	Stress at 200 Strain (N/mm2)	Stress at 300 Strain (N/mm2)
P1-0-0	8,83	11,17	18,6
P2-450-2.5	9,71	12,36	19,02
P3-450-5.0	9,26	11,555	18,23
P4-250-2.5	9,315	11,825	18,675
P5-250-5.0	9,445	11,795	17,925
P6-8-2.5	9,225	11,69	17,01
P7-8-5.0	9,345	11,645	15,87
P8-4-2.5	8,97	11,85	15,6
P9-4-5.0	9,445	11,965	17,51

Table B.1: MFI Results of TPU/PTFE Blends

Sample code	MFI (g/10mins)
P1-0-0	16.829±0.197
P2-450-2.5	13.272±0.056
P3-450-5.0	12.007±0.055
P4-250-2.5	14.690±0.680
P5-250-5.0	13.146±0.059
P6-8-2.5	14.443±0.058
P7-8-5.0	14.148±0.060
P8-4-2.5	16.349±0.072
P9-4-5.0	15.876±0.087

CURRICULUM VITAE

He was born 1978 in Istanbul. He graduated from Ahmet Simsek Science High School in 1994 and attempted to Chemical Engineering Department of I.T.U in 1996. In 2001, he graduated from university. He worked for Flokser A.Ş. as R&D engineer, Product Manager and Technical Sales Representative for USA and North Europe between 2002 and 2006. He worked for Depar Deri Plastik A.Ş. as Technical Sales Manager between 2006 and 2009. He worked for Gemsan A.Ş as Speciality Chemicals Business Unit Manager between 2009 and 2010. He is now working for Enpas Plastik/Ravago as Technical Sales and Marketing Engineer since 2010. He was accepted as a master student to Istanbul Technical University, Polymer Science and Technology interdisciplinary graduate programme.